Chapter 3

Preparation and Characterization of Ion-Exchange Membranes

1 INTRODUCTION

Key components in ion-exchange membrane separation processes are membranes which are used in various applications. Their properties determine to a large extent the technical feasibility and the economics of the processes. A significant amount of work has been concentrated over the last 50 years in academic institutions as well as in industry to develop efficient membranes with high permeability, good permselectivity for certain ionic components and a long useful life under operating conditions. This work is documented in a very large number of publications and especially in patents which describe in great detail preparation procedures [R. Kunin, 1958], [F. Bergsma et al., 1961], [F. Helfferich, 1962], [N.P., Suryanarayana, et al., 1963] and [T. Sata,. 1986]. With the development of the low temperature polymer electrolyte fuel cell to be used for the methanol direct conversion in mobile applications the interest in new ion-exchange membranes with special properties such as low methanol permeability has drastically increased [J. Kerres et al., 2001].

Due to the importance of the membranes in electrodialysis and related processes it is not surprising that there are numerous detailed recipes described mainly in the patent literature for the manufacturing of ion-exchange membranes with special application adjusted properties. The preparation procedures of ion-exchange membranes are closely related to those of ion-exchange resins [E.B. Tooper et al., 1956]. As with resins, there are many possible types with different polymer matrixes and different functional groups to confer ion-exchange properties on the product. Although there are a number of inorganic ion-exchange materials [F. Helfferich, 1962] most of them are based on zeolites, zirconium phosphates, and bentonites. These materials are rather unimportant today in electrodialysis and related processes with the exception of the high temperature fuel cell which will not be discussed further.

Ion-exchange membranes can be classified by their function as a separation media or according to their structure and basic material. As far as their function is concerned ion-exchange membranes may be classified as:

- cation-exchange membranes which contain fixed negatively charged ions and which have a selective permeability for cations,
- anion-exchange membranes which contain fixed positively charged ions and which have a selective permeability for anions,
- amphoteric ion-exchange membranes in which both negatively and positively fixed ionic groups are randomly distributed,
- bipolar membranes which consist of a cation- and an anion-exchange membrane laminated together ,
- mosaic ion-exchange membranes which are composed of macroscopic domains of polymers with negatively fixed ions and those with positively fixed ions randomly distributed in a neutral polymer matrix.

The structure of an ion-exchange membrane based on a polymer matrix and fixed charge groups are illustrated in Figure 3.1.

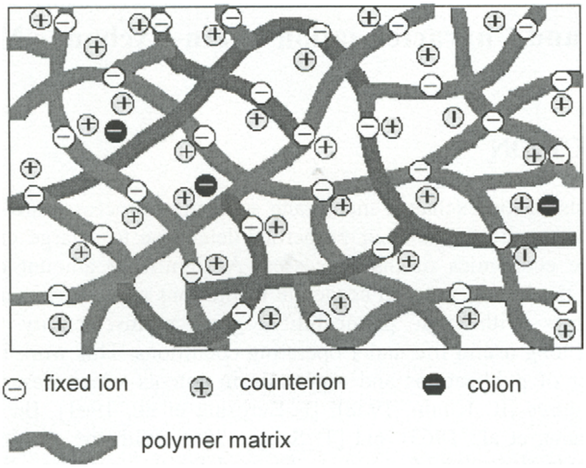


Fig. 3.1 Schematic drawing illustrating the structure of a cation-exchange membrane.

This figure shows schematically the matrix of a cation-exchange membrane with fixed anions and mobile cations, which are referred to as counterions. In contrast, the mobile anions, called coions, are more or less completely excluded from the polymer matrix because of their electrical charge which is identical to that of the fixed ions. Due to the exclusion of the co-ions, an ideal cation-exchange membrane permits transfer of cations only. Ideal anion-exchange membranes carry positive charges fixed on the polymer matrix. Therefore, they exclude all cations and are permeable to anions only.

The most desired properties for ion-exchange membranes are:

- high permselectivity - an ion-exchange membrane should be highly permeable for counterions, but should be impermeable to coions,
- low electrical resistance - the permeability of an ion-exchange membrane for the counterions under the driving force of an electrical potential gradient should be as high as possible,
- good mechanical and form stability - the membrane should be mechanically strong and should have a low degree of swelling or shrinking in transition from dilute to concentrated ionic solutions,
- high chemical stability - the membrane should be stable over the entire pH-range and in the presence of oxidizing agents.

It is often difficult to optimize the properties of ion-exchange membranes because the parameters determining the different properties often act contrary to each other. For instance, a high degree of cross-linking improves the mechanical strength of the membrane but also increases its electrical resistance. A high concentration of fixed ionic charges in the membrane matrix leads to a low electric resistance but, in general, causes a high degree of swelling combined with poor mechanical stability. The properties of ion-exchange membranes are determined by two parameters, namely the basic material they are made from and the type and concentration of the fixed ionic moiety. The basic material determines to a large extent the mechanical, chemical, and thermal stability of the membrane [P. Meares, 1983], [K.S. Spiegler, et al., 1980]. Based on the material of the ion-exchange membranes they can be classified as:

- membranes composed of hydrocarbon or partially halogenated hydrocarbon polymers,
- membranes composed of perfluorocarbon polymers,
- membranes made from inorganic materials,
- membranes composed of inorganic ion-exchange material and an organic polymer.

In most commercially available ion-exchange membranes the matrix consists of hydrophobic polymers such as polystyrene, polyethylene or polysulfone. Although these basic polymers are insoluble in water and show a low degree of swelling, they may become water soluble by the introduction of the ionic moieties. Therefore, the polymer matrix of ion-exchange membranes is very often cross-linked. The degree of cross-linking then determines to a large extent the degree of swelling and the chemical and thermal stability, but it also has a large effect on the electrical resistance and the permselectivity of the membrane.

The type and the concentration of the fixed ionic charges determine the permselectivity and the electrical resistance of the membrane, but they also have a significant effect on the mechanical properties of the membrane. The degree of swelling, especially, is effected by the concentration of the fixed charges.

The following moieties are used as fixed charges in cation-exchange membranes:

$-SO_3^-, \quad -COO^-, \quad -PO_3^{2-}, \quad -PHO_2^-, \quad -AsO_3^{2-}, \quad -SeO_3^-.$

In anion-exchange membranes fixed charges may be:

$-\overset{+}{N}H_2R, \quad -\overset{+}{N}HR_2, \quad -\overset{+}{N}R_3, \quad -\overset{+}{P}R_3, \quad -\overset{+}{S}R_2$

These different ionic groups have significant effects on the selectivity and electrical resistance of the ion-exchange membrane. The sulfonic acid group, e.g. $-SO_3^-$ is completely dissociated over nearly the entire pH-range, while the carboxylic acid group $-COO^-$ is virtually undissociated in the pH-range < 3. The quaternary ammonium group $-\overset{+}{N}R_3$ again is completely dissociated over the entire pH-range, while the secondary ammonium group $-\overset{+}{N}H_2R$ is only weakly dissociated. Accordingly, ion-exchange membranes are referred to as being weakly or strongly acidic or basic in character. Most commercially available ion-exchange membranes have $-SO_3^-$ or $-COO^-$ groups, and most anion-exchange membranes contain $-R_3\overset{+}{N}$ groups.

Ion-exchange membranes can also be divided, according to their structure and preparation procedure, into two major categories: homogeneous membranes and heterogeneous membranes [F. Bergsma et al., 1961].

In homogeneous ion-exchange membranes the fixed charged groups are evenly distributed over the entire membrane polymer matrix. Homogeneous membranes can be produced, e.g. by polymerization or polycondensation of functional monomers such as phenolsulfonic acid with formaldehyde [F. Helfferich, 1962], or by functionalizing a polymer such as polysulfone dissolved in an appropriate solvent by sulfonation and cast into a film [P. Zschocke et al., 1985].

Heterogeneous ion-exchange membranes have distinct macroscopic domains of ion-exchange resins in the matrix of an uncharged polymer. They can be produced by melting and pressing of a dry ion-exchange resin with granulated polymer such as polyvinylchloride, or by dispersion of the ion-exchange resin in a polymer solution [G.E. Molau, 1981].

The completely homogeneous and the macroscopically heterogeneous ion-exchange membranes are extreme structures. Most ion-exchange membranes show a certain degree of heterogenity on the microscopic scale. The degree of heterogenity of ion-exchange membranes increases according to the following order [T. Sata, 1986]:

- homogeneous ion-exchange membranes,
- interpolymer membranes,
- microheterogeneous graft- and block-polymer membranes,
- snake-in-the-cage ion-exchange membranes, and
- heterogeneous ion-exchange membranes.

From the viewpoint of macromolecular chemistry all the intermediate forms may be considered as so-called polymer blends. As a consequence of the polymer/polymer incompatibility a certain phase separation of the different polymers and a specific aggregation of the hydrophilic and hydrophobic domains is obtained. A classification of the membrane morphology according to the type and the size of the microphase is possible. If membranes are translucent their structure is homogeneous or they contain inhomogenities that are smaller than the wavelength of visible light (400 nm). Thus, these membranes are called interpolymer or microheterogeneous membranes. Microheterogeneous membranes for example are produced by means of block-copolymerization of ionogenic and non-ionogenic monomers, or by graft-copolymerization of functional monomers [J. A. Kerres, 2000]. Interpolymer membranes are produced by dissolving compatible, functional polymers such as sulfonated polyetherketon and polysulfone in one solvent to form a homogeneous, macroscopically transparent solution, followed by the evaporation of the solvent [W. Cui et al., 1998].

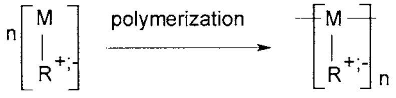
2 PREPARATION OF ION-EXCHANGE MEMBRANES

As far as their chemical structure is concerned ion-exchange membranes are very similar to normal ion-exchange resins; from the chemical point of view, these resins would make excellent membranes of high selectivity and conductivity. The difference between membranes and resins arises largely from the mechanical requirements of the membrane process. Unfortunately, ion-exchange resins are mechanically weak, cation-exchange resins tend to be brittle and anion-exchange resins to be soft [F. Helfferich, 1962]. They are dimensionally unstable due to the variation in the amount of water imbibed into the gel under different circumstances. Changes in electrolyte concentration, in the ionic form or in temperature may cause major changes in the water uptake and hence in the volume of the resin. These changes can be tolerated in small spherical beads, but in large sheets which have been cut to fit an apparatus they are not acceptable. Thus, it is generally not possible to use sheets of material which has been prepared in the same way as a bead resin. The most common solution to this problem is the preparation of a membrane with a backing of a stable reinforcing material which gives the necessary strength and dimensional stability. Preparation procedures for making ion-exchange resins and membranes are described in great detail in the patent literature [A. A. Kasper, 1955], [W. Juda et al., 1950, 1953], [K. Haagen et al.,1959], [W.G. Grot, 1974, 1975], and [Y. Onoue et al., 1980], [S.R. Caplan et al., 1974], [D.S. Flett, 1983].

2.1 Preparation of Homogeneous and Microheterogeneous Membranes

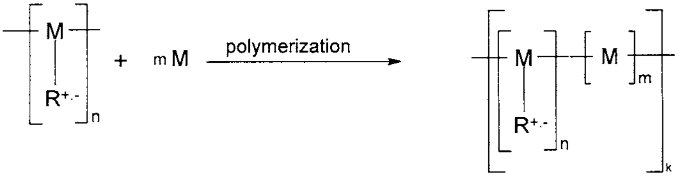
The definition of homogeneous ion-exchange membranes used here includes micro-heterogeneous structures such as inter-polymers, graft-, block- and co-polymers. The different techniques of the preparation of ion-exchange membranes can be schematically illustrated as:

- Polymerization of monomers that contain a moiety that either is or can be made anionic or cationic, respectively:



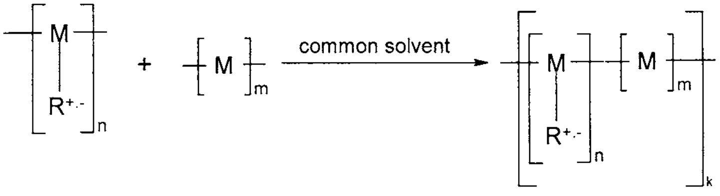
Membranes prepared by this technique often show a rather high charge density which is fixed by the molecular weight of the monomer and show excessive swelling.

- Polymerization of a monomer that contains an anionic or a cationic moiety with a neutral polymer:



By co-polymerization of a monomer containing a positive or negative charge with a neutral monomer the fixed charge density can easily be controlled by the ratio of the two monomers.

- Preparation of block polymers or polymer mixtures of a neutral polymer with polymer containing anionic or cationic moieties:



By preparing block polymers or mixtures of neutral and electric charges carrying polymers ion-exchange membranes with well controlled properties concerning the electrical charge density or hydrophilic and hydrophobic character can easily be prepared.

- Introduction of anionic or cationic moieties into a polymer dissolved in a solvent by a chemical reaction such as sulfonation with sulfuric acid or chlorosulfonic acid:

$$\text{polymer-Y} + \text{X-R}^{+,-} \xrightarrow{\text{chemical reaction}} \text{polymer-R}^{+,-} + \text{X-Y}$$

Here polymer-Y presents a polymer with a reactive end group Y while $\text{X-R}^{+,-}$ is a charge group containing reagent such as chlorosulfonic acid.

This is a very simple method to introduce electrical charges into a polymer matrix and to prepare an ion-exchange membrane by casting a film of the modified polymer and evaporating the solvent. However, the degree of functionalization is often difficult to control.

- Introducing functional groups into a preformed polymer film by grafting:

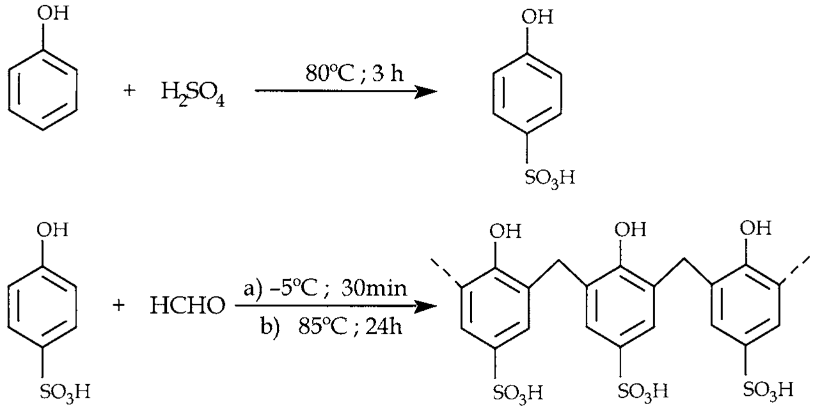
$$\text{polymer} + \text{M-R}^{+,-} \xrightarrow{\text{irradiation, plasma}} \text{polymer-M-R}^{+,-}$$

Here $\text{M-R}^{+,-}$ is a charge group containing monomer.

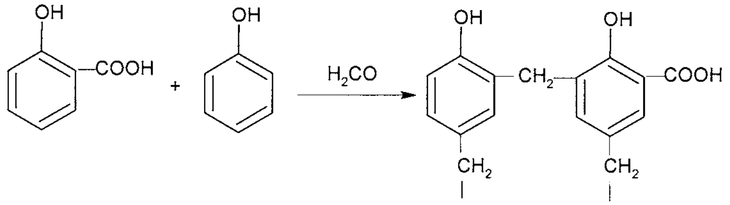
In this method of preparing ion-exchange membranes a polymer, that is not readily soluble in a common solvent such as a polytetrafluorethylene film, is exposed to a monomer carrying the desired functional group and then irradiated or plasma treated. While the actual process is simple the degree of functionalization of the polymer is difficult to control and often very heterogeneous structures are obtained.

2.1.1 Polymerization and Polycondensation of Monomers

The literature contains a multitude of detailed recipes for making ion-exchange resins and membranes by polymerization. Some of these preparation procedures shall briefly be described. One of the first membranes made by polymerization or polycondensation of monomers was prepared from phenol by polycondensation with formaldehyde. In the first step an ion-exchange resin is prepared which then is converted into a membrane. For the preparation of the resin phenol is treated with concentrated H_2SO_4 at 80°C for about 3 hours which leads to the phenolsulfonic acid in para position, a brown, crystalline material. This acid is reacted with a 38%-solution of formaldehyde in water initially at -5°C for about 30 minutes and then at 85°C for several hours. The solution is then cast into a film which solidifies when the solution is cooled down to room temperature. Excess monomer is removed by washing the film with water. Since the sulfone group is directly bound to the benzene ring a strong acid type ion-exchange resin is obtained which is completely dissociated over the entire pH-range [N. Ishibashi et al., 1954], [F. Helfferich, 1962], [W.A. McRae et al., 1960]. The reaction is shown in the following scheme:



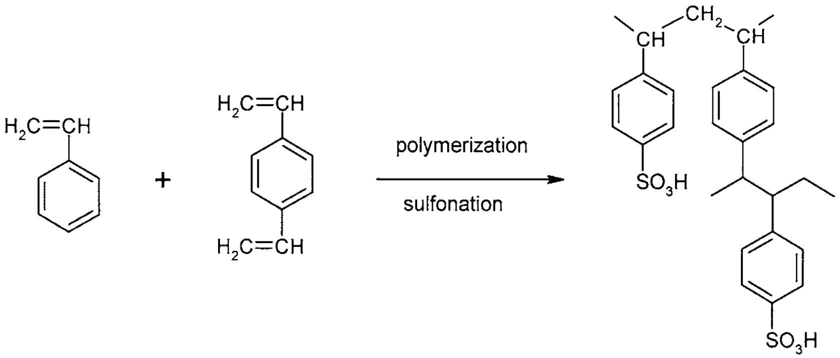
A weak ion-exchange membrane is obtained when instead of phenolsulfonic acid, e.g. salicylic acid is reacted with phenol and formaldehyde according to the following reaction scheme:



These films, however, are chemically and mechanically not very stable and are difficult to handle without a proper support material.

A method of preparing both cation- and anion-exchange membranes, which is widely used for the preparation of commercial membranes, is the polymerization of styrene and divinylbenzene and its subsequent sulfonation or amination.

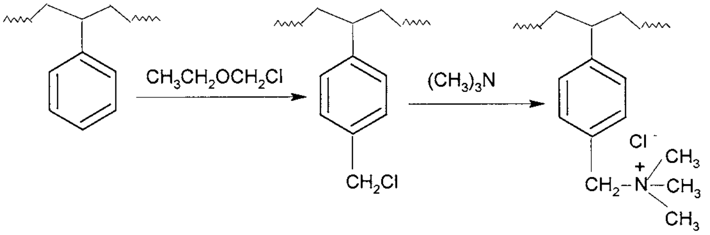
The cation-exchange membrane is obtained according to the following reaction scheme [K. Kusomoto et al., 1976]:



In a first step styrene is partially polymerized with divinylbenzene at about 60°C using benzoyl peroxide as an initiator for the polymerization. The polymer is partially cross-linked and obtained as a block which is cut into slices and in a second step sulfonated with concentrated sulfuric acid at room temperature. The obtained membranes show high ion-exchange capacity and low electrical resistance but their mechanical strength is insufficient to be used without a proper support material.

However, by addition of linear polymers such as polyvinylchloride, polyethylenestyrene-butadiene rubber, etc. to a mixture of styrene, divinylbenzene, and a plasticizer a pasty mixture is obtained. The mixture is then coated on a fabric backing such as a net and covered on both sides with a glass plate or a separating plastic sheet of polyvinylalcohol or polyethylene-terephtalate. By heating the composite layer vinyl monomers, divinylbenzene, peroxides, and additives are polymerized. The obtained film is then sulfonated with concentrated sulfuric acid as described earlier. The result is a reinforced ion-exchange membrane with excellent electrical and mechanical properties. Many of the commercial hydrocarbon-type ion-exchange membranes marketed by Tokuyama Soda and Asahi Glass are manufactured this way today [Asahi Glass, 1990].

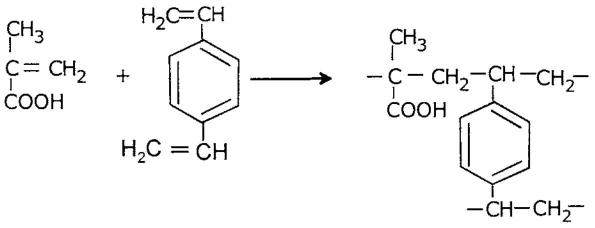
A homogeneous anion-exchange membrane can be obtained by introducing a positively charged quaternary amine group into a preformed polymer by a chloromethylation procedure followed by an amination with a tertiary amine according to the following reaction scheme:



Membranes with good electrical and mechanical properties were obtained by additional polymerization with divinylbenzene or by first polymerizing the monochloromethylstyrene with divinylbenzene and then treating the resulting polymeric film with trimethylamine.

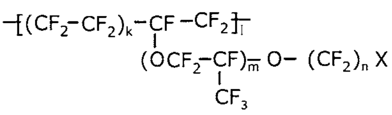
The membrane structures and their preparation described above are just two examples. There are many variations of the basic preparation procedure resulting in slightly different products. Instead of styrene often substituted styrenes such as methylstyrene or phenylacetate are used and instead of divinylbenzene monomers such as divinylacetylene or butadiene are used. Furthermore, instead of sulfonic acid phoposphoric or arsenic acid is introduced in the cross-linked polystyrene. However, most of these membranes have no, or only very little commercial relevance.

In most ion-exchange membranes based on polystyrene the ion-exchange moiety is introduced into the cross-linked polymer. This preparation technique has the disadvantage that the degree of sulfonation is difficult to control. In principle the monomers can be sulfonated prior to polymerization and cross-linking. By adjusting the ratio of sulfonated to non-sulfonated monomers the desired degree of sulfonation in the final membrane can be controlled. There are several detailed recipes described in the literature. A typical example is the preparation of a weak acidic ion-exchange membrane by cross-linking methacrylic acid with divinylbenzene according to the following reaction scheme:



Numerous references exist in the literature for the preparation of ion-exchange membranes by polymerization. One of the technically and commercially most important cation-exchange membrane developed in recent years is based on perfluorocarbon polymers. Membranes of this type have extreme chemical and thermal stability and they are the key component in the chloralkali electrolysis and in most of today's fuel cells [A. Eisenberg et al., 1982]. They are prepared by copolymerization of tetrafluoroethylene with perfluorovinylether having a carboxylic or sulfonic acid group at the end of a side chain. There are several variations of a general basic structure commercially available today. The properties of these membranes have been optimized over the years with its special application in the chlorine-alkaline industry in mind. The various preparation techniques are described in detail in the patent literature [D.J. Connolly et al., 1966], [W.G. Grot, 1973, 1974] and [M.S. Seko et al., 1988].

Today's commercially available perfluorocarbon membranes have the following basic structure:



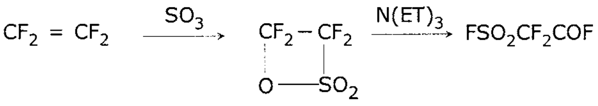
$$-[(CF_2-CF_2)_k-CF(-(OCF_2-CF(CF_3))_m-O-(CF_2)_n X)-CF_2]_l-$$

$k = 5\text{-}8,\ l = 600\text{-}1200,\ m = 1\text{-}2,\ n = 1\text{-}4,\ X = SO_3^-\ ,\ COO^-$

The synthesis of the perfluorocarbon membranes is rather complex and requires a multistep process. Several companies have developed synthesis routes, however, the differences in the final structures are relatively small. One of the earliest publications describes a route developed by DuPont in the 70'ties [W.G. Grot, 1973, 1974]. It contains 4 mayor steps:

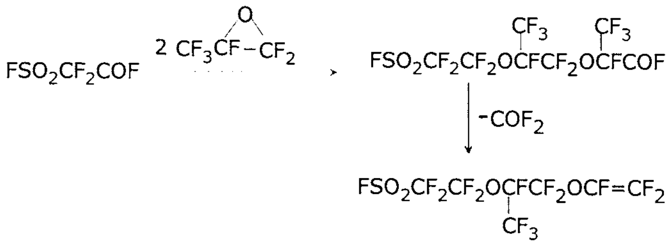
1. Synthesis of the sulfonated monomer

The first step is a reaction of tetrafluoroethylene with sulfur trioxide followed by a ring opening of cyclic product to form the fluorosulfonylacetylfluoride according to the following reaction scheme:



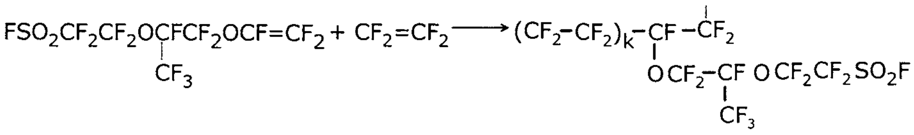
2. Synthesis of the polyvinylethersulfonylfluoride

In the second step the fluorosulfonylacetylfluoride is heated with sodium carbonate and the polyvinylethersulfonyl fluoride is formed according to the following reaction scheme.



3. Formation of the fluorocarbonvinylether resin

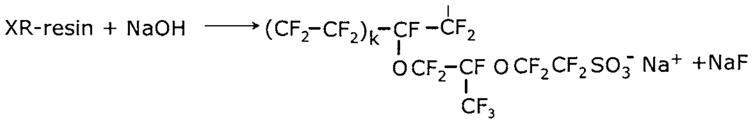
In the third step the vinylether is copolymerized with tetrafluoroethylene to form a neutral thermoplastic polymer which can be extruded in sheet form. This polymer is generally referred to as XR-resin.



$$\mathrm{FSO_2CF_2CF_2O\underset{\substack{|\\ CF_3}}{C}FCF_2OCF{=}CF_2 + CF_2{=}CF_2 \longrightarrow (CF_2{-}CF_2)_k{-}\underset{\substack{|\\ OCF_2-\underset{\substack{|\\ CF_3}}{C}F\ OCF_2CF_2SO_2F}}{C}F{-}\overset{|}{C}F_2}$$

4. Conversion of the XR-resin to an ion-exchange membrane

The last step in the preparation of the final membrane is the conversion of the neutral XR-resin sheet into a negatively charged cation-exchange membrane. This is done by a treatment with hot sodium hydroxide according to the following reaction scheme:

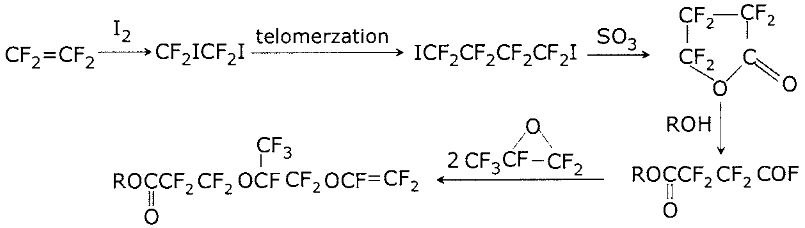


$$\mathrm{XR\text{-}resin + NaOH \longrightarrow (CF_2{-}CF_2)_k{-}\underset{\substack{|\\ OCF_2-\underset{\substack{|\\ CF_3}}{C}F\ OCF_2CF_2SO_3^-\ Na^+}}{C}F{-}\overset{|}{C}F_2 + NaF}$$

The sodium counter-ion in the membrane can readily be exchanged for other cations by immersing the film into the appropriate aqueous solution.

Perfluorinated membranes have excellent chemical and thermal stability. But because of the strong acidity and high hydrophilicity of the perfluorosulfonic group the membrane shows a high degree of swelling which results in a low electric resistance but also in relatively poor permselectivity, since excessive swelling can produce water filled channels which permit the passage of co-ions. The degree of swelling is also a function of the fixed ion concentration, i.e. the equivalent weight of the polymer, which is typically between 600 and 1500 grams of dry polymer per mol of ion-exchange site. Thus, the ion-exchange capacity of the membrane is between 0.5 to 2 milliequivalent per gram. The degree of swelling could be reduced by reducing the ion-exchange capacity of the membrane. This, however, would increase the electrical resistance and reduce the permselectivity in concentrated electrolyte solutions because of the decrease in the Donnan exclusion. The permselectivity of the membrane in concentrated electrolyte solutions is therefore often unsatisfactory [M.V. Coulter, 1980].

To improve the overall performance of the membrane or to adapt it to certain applications various modifications of the basic polymer have been introduced mainly to change the ion-exchange groups either of the entire membrane or only at its surface. In addition to the $-SO_3H$ group, carboxylic acid –COOH, sulfonamide $-SO_2(CH_2)NH_2$, or quaternized alcohol groups -COH are used in commercial membranes. Ion-exchange membranes with carboxcylic acid as charged group have significantly lower water sorption and, thus, higher permselectivity but also drastically increased electrical resistance. Because of the weak acidic character of the carboxylic acid group perfluorocarboxylate membranes may either be prepared from the appropriate monomers or by replacing the sulfonic acid group in the polymer by a carboxylic acid group. The second method is used mainly for the modification of the membrane surface. The $-CF_2SO_2F$ groups are converted to –COOH groups in various ways by the different manufacturers [Y.T. Onoue et al., 1980]. Tokuyama Soda Co. transforms the $-CF_2SO_3H$ groups to $-CF_2SO_2Cl$ with a solution of phosphorepentachloride which then is reduced to sulfinic acid by reaction with hydrazine and hence oxidizes to –COOH. Homogeneous perfluorocarboxylic acid membranes can be prepared by different routes. Asahi Chemical produces the carboxylic acid monomers from tetrafluoroethylene according to the following scheme:



By addition of iodine to the tetrafluoroethylene, telomerization and oxidation by SO_3 a cyclic compound is obtained. Further treatment with alcohol leads to a ring opening and the formation of a bifunctional component which is then reacted with hexafluoropropylene epoxide to form the carboxalfluorodevinylether. The copolymerization of the monomer with tetrafluoroethylene leads to the thermoplastic polymer as described previously.

The synthesis of the bifunctional compounds $RCOO-(CF_2)_n-COF$ and $SO_2F-(CF_2)_n-COF$ is the key step in the entire membrane production process. Copolymerization of the functionalized monomers with hexafluoropropylene epoxide and tetrafluoroethylene are comparatively simple procedures.

The perfluorinated cation-exchange membrane is today by far the commercially most relevant membrane with applications not only in the chlorine-alkaline industry but also in fuel cells, electrolysis, and electrodialysis of certain industrial effluents. In recent years an entire series of modifications have been introduced in the original membrane manufacturing process to adapt the properties of the membrane to the anticipated practical application and today a number of perfluorinated membranes are commercially available which are quite different in their structure and electrochemical properties [H.L., Yeager, 1982].

In the electrolytic chlorine and alkaline production often perfluorinated membranes are used which contain a thin layer of a resin with the weakly acidic carboxylic acid group on a core resin containing the strongly acidic sulfonic acid group. These membranes are made either by lamination or by surface treatment according to the scheme of Figure 3.2.

For fuel cells used in the methanol direct conversion perfluorinated cation-exchange membranes having a low methanol permeability are being developed to avoid excessive methanol loss.

Asahi Chemical, Dupont and others are producing today both homogeneous and laminar perfluorocarboxylic acid membranes [R.L. Dotson et al., 1982], [T. Sata et al., 1983], [Tokuyama Soda Product Bulletin, 1988] and [Asahi Chemical Product Bulletin, 1988].

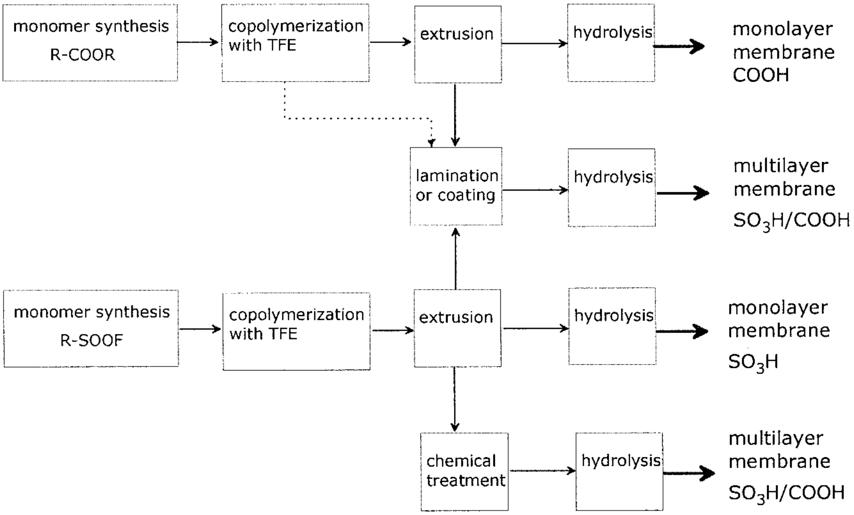
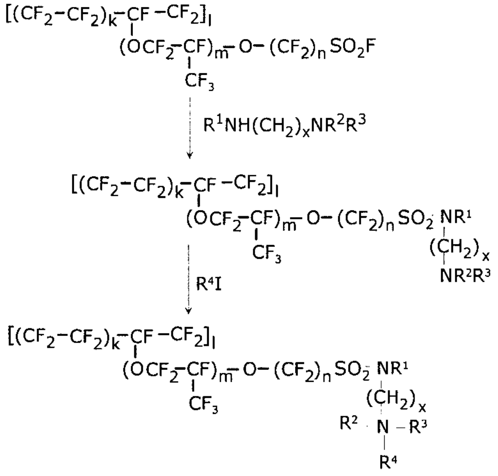


Fig. 3.2 Schematic diagram of the different pathways for the preparation of mono- and multi-layer fluorocarbon ion-exchange membranes.

In addition to the various perfluorinated cation-exchange membranes also an anion-exchange membrane can be prepared according to the following scheme [K.E. Matsui et al., 1986]:



The preparation is based on the reaction of the sulfonylfluoride polymer with a diamine to a sulfonamide with a pendant amine group which then further reacts with an alkyl iodine to a quaternary amine. according to the following scheme [K.E. Matsui et al., 1986]:

The anion-exchange membrane is quite stable at elevated temperature up to 120°C in an oxidizing environment as well as in strong acids and bases. However, in spite of excellent chemical stability the perfluorinated anion-exchange membrane has not reached nearly the commercial relevance as the cation-exchange membrane.

2.1.2 Introduction of Ionic Groups into a Preformed Solid Polymer Film

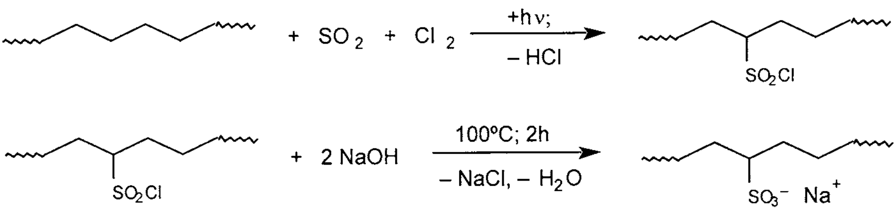
Concerning the introduction of anionic or cationic moieties into a preformed film two techniques are applied:

1. A film of a commercial polymer such as polyethylene, polyvinylchloride or polytetrafluoroethylene is swollen with a monomer such as divinylbenzene. Then the monomers are polymerized with the film which also contains a radical initiator [I. Ishigaki et al., 1978]. Alternatively, a vinyl monomer may be grafted onto a polymer film by radiation techniques. The film is exposed to X-rays to form radicals in the polymer matrix which bind the vinyl monomer. Ion-exchange groups are then introduced by sulfonation, or chloromethylation, and amination. Starting with a film makes the membrane preparation rather easy. The starting material may be a hydrophilic polymer, such as cellophane or polyvinylalcohol. More often, however, a hydrophobic polymer such as polyethylene or polystyrene is used. In recent years a large number of papers have been published on the preparation of ion-exchange membranes by this method. However, the commercial success is rather limited.

2. A film of a commercial polymer such as polyethylene or polypropylene is directly sulfonated or aminated. A typical example is the preparation of ion-exchange membranes by sulfochlorination and amination.

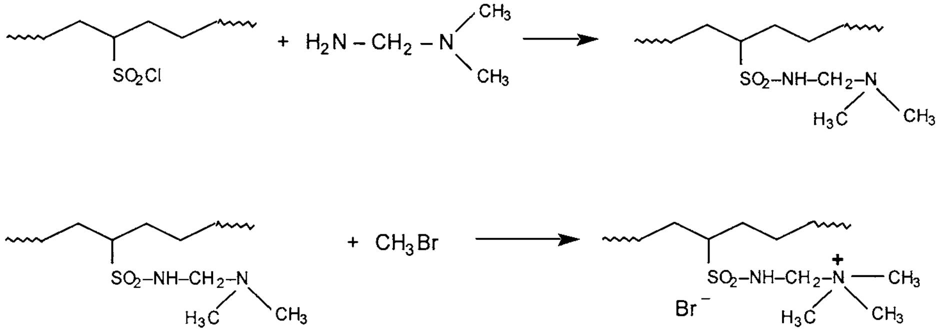
a) Preparation of the cation-exchange membrane

Exposure of a polyethylene film to a mixture of SO_2 and Cl_2 gases under an UV-light source results in the sulfochloronation of the polymer [E. Korngold, 1984], [F. De Korocy et al., 1967]. The membrane is then reacted with sodiumhydroxide to hydrolyse the sulfonylchloride group to sodiumsulfonate resulting in a cation-exchange membrane according to the following reaction scheme:



b) Preparation of the anion-exchange membrane

Alternative reaction with a diamine which contains both primary and tertiary amino groups results in an acid amide bonding. The pendant tertiary amine is quaternized with methylbromide resulting in an anion-exchange membrane.



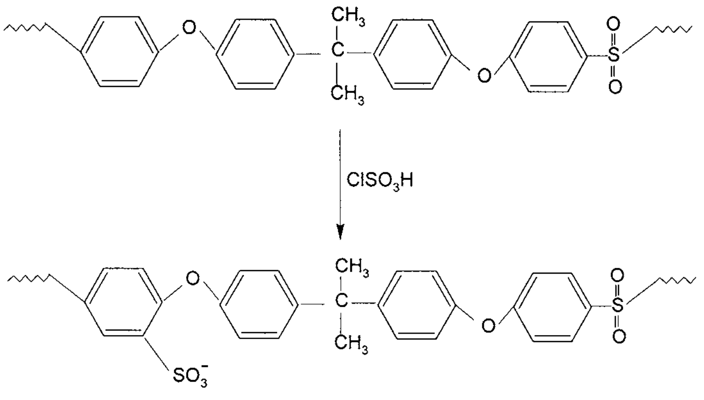
Ion-exchange membranes prepared by this method from polyethylene sheets have low electrical resistance combined with high permselectivity and excellent mechanical strength. However, in spite of their good properties these membranes are no longer commercially available.

2.1.3 Introduction of Ionic Groups into a Dissolved Polymer

Membranes can also be prepared by dissolving and casting a functionalized polymer, such as sulfonated polysulfone, sulfonated polyetheretherketone or polyphenyleneoxide into a film. As a typical example the preparation of a cation- and anion-exchange membrane based on polysulfone is described in the following reaction schemes.

Preparation of a cation-exchange membrane by sulfonation of polysulfone

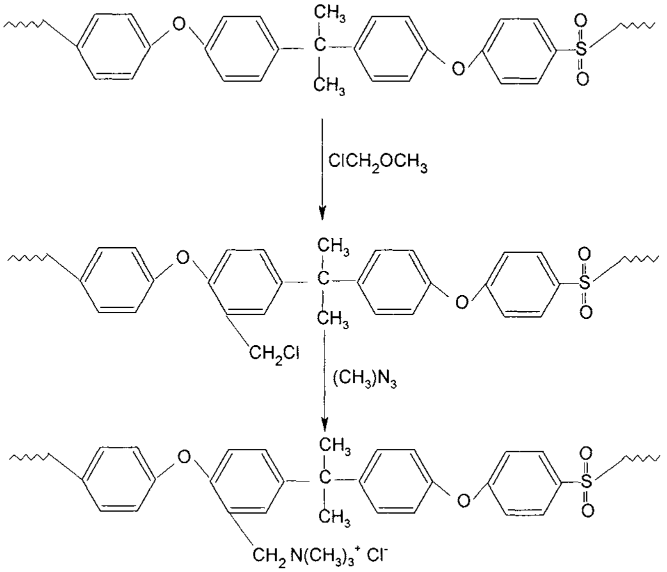
The sulfonation is carried out with chlorosulfonic acid according to the following scheme:



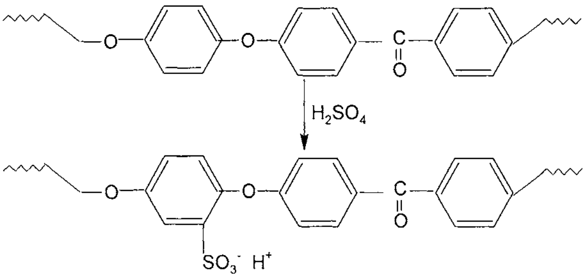
The sulfonated polysulfone can be cast as a film on a screen and precipitated after the evaporation of most of the solvent such as dichloroethane. This leads to a reinforced membrane with excellent chemical and mechanical stabilities and good electrochemical properties [P. Zschocke et al., 1985].

Preparation of the anion-exchange membrane based on polysulfon

The anion-exchange membrane based on polysulfone is prepared by halomethylation of the backbone polymer and subsequent reaction with a tertiary amine as follows:



For the preparation of cation-exchange membranes also polyetheretherketone is used as the basic polymer. It can very easily be sulfonated with concentrated sulfuric acid according to the following scheme:



The sulfonation occurs on one polyetheretherketone block only and is thus very easy to control. To obtain membranes with different ion-exchange capacity the sulfonated polyetheretherketone can be mixed with polyethersulfone in a solvent such as N-methylpyrrolidone. By changing the ratio of the sulfonated polyetheretherketone to polyethersulfone the fixed charge density can easily be adjusted to a desired value [F.W. Wilhelm, 2001].

2.2 Preparation Procedure of Heterogeneous Ion-Exchange Membranes

Ion-exchange membranes with a heterogeneous structure consist of fine ion-exchange particles embedded in an inert binder such as polyethylene, phenolic resins, or polyvinylchloride. Heterogeneous ion-exchange membranes are characterized by the discontinuous phase of the ion-exchange material. The efficient transport of ions through a heterogeneous membrane requires either a contact between the ion-exchange particles or an ion conducting solution between the particles. Heterogeneous ion-exchange membranes can easily be prepared by different methods:

- An ion-exchange powder is mixed with a dry binder polymer and molded under the appropriate conditions of pressure and temperature into a sheet.
- Ion-exchange particles are mixed with a binder polymer which is brought into a semi-fluid state by adding a plasticizer or by heating and then extruded as a sheet.
- Ion-exchange particles are dispersed in a solution containing a dissolved film-forming binder, then the mixture is cast into a film and the solvent evaporated.
- Similarly, ion-exchange particles are dispersed in a partially polymerized binder polymer and cast into a film, then the polymerization is completed.

The size of the ion-exchange particles in the membranes made by the above described preparation procedures is generally below 50μm. Heterogeneous ion-exchange membranes with useful low electrical resistances contain more than 65% by weight of the ion-exchange particles. Since these ion-exchange particles swell when immersed in water, it is difficult to achieve adequate mechanical strength combined with low electrical resistance. Most heterogeneous membranes that possess adequate mechanical strength generally show poor electrochemical properties. On the other hand, a membrane that contains ion-exchange particles in a concentration high enough to show the desired electrochemical performance often exhibits poor mechanical strength. Furthermore, it has been shown that heterogeneous membranes with an ion-exchange resin content equivalent to that of a homogeneous ion-exchange membrane exhibit a greater degree of swelling when immersed in water than would be expected from the density of the wet ion-exchange material and the binder polymer. Apparently those membranes develop water filled interstices during the swelling process. This results not only in poor mechanical properties but also poor permselectivity.

However, there are significant differences between ion-exchange membranes and ion-exchange resins concerning the polymer structures which are primarily due to the differences in size and shape between ion-exchange beads and ion-exchange membrane sheets. In both cases the fixed ion-exchange groups lead to a swelling of the polymer when it is in contact with an aqueous solution. The degree of swelling depends on the ionic strength of the solution and on the degree of cross-linking of the polymer. Due to the spherical symmetry of granular ion-exchange resins and due to the fact that they are not physically constrained in use, there is generally no functionally important physical damage to the resins from drying and rewetting or from changes of the ambient ionic strength.

Dimensional changes which are tolerable during use in the case of granular ion-exchange resins, however, are not acceptable in ion-exchange membranes due to the large sizes of the latter and the fact that they are physically constrained in the electrodialysis stacks in which they are used. As a result, the ion-exchange capacities of ion-exchange membranes are about 1–3 equivalent per kilogram of dry membrane and thus significantly lower than that of a granular ion-exchanger resin which is 3–5 equivalent per kilogram dry resin, a fact that results in a reduced swelling of ion-exchange membranes compared to resins. In addition to covalent cross-linking of polymers other strategies are used to limit swelling by using, e.g. reinforcing fabrics, or by including polymer segments in the ion-exchange resin polymers which yield microcrystalline regions in the resins.

In general, heterogeneous ion-exchange membranes have relatively high electrical resistances. Homogeneous ion-exchange membranes have a more even distribution of fixed ions and often lower electrical resistances.

2.3 Special Property Ion-Exchange Membranes

Generally, cation-exchange membranes are permeable for cations and more or less impermeable for anions, while anion-exchange membranes are permeable to anions and more or less impermeable for cations. A separation of cations from anions is therefore quite efficient in electrodialysis. In other electromembrane processes such as diffusion dialysis and electrodialysis with bipolar membranes or specific application of electrodialysis, e.g. in the production of table salt from sea water or the removal of nitrate from potable water, additional properties such as the selectivity for ions of the same electrical charge may be required [Y. Kobuchi, et al., 1987], [G. Pourcelly et al., 1994]. Significant effort has also been concentrated on the development of anion-exchange membranes with low fouling, i.e. adsorption of high molecular weight charged materials, tendencies, and high chemical and thermal stability. In addition to excellent chemical stability and ion permselectivity bipolar membranes must exhibit high water dissociation capability and low electric resistance to be useful in practical applications. In the literature, there are numerous methods reported for the preparation of ion-exchange membranes with special properties to be used in the chemical process industry, for the treatment of industrial effluents, or as battery separators and ion-selective electrodes.

2.3.1 Monovalent Ion Permselective Membranes

Since 1972, in Japan table salt is produced by electrodialytic concentration of sea water. For the specific requirements of this process, ion-exchange membranes have been developed which can separate to a large extent monovalent ions from a solution mixed with multivalent ions. An increase in the cross-linking density of a cation-exchange membrane or the formation of a thin layer of a highly cross-linked resin on a low cross-linked cation-exchange membrane [Y. Onoue et al., 1961] results in a significant increase in permeability of monovalent over multivalent cations. The introduction of a small amount of anion-exchange groups in a cation-exchange membrane or the formation of a thin layer of a positively charged polyelectrolyte on the surface of a cation-exchange membrane also increases the membrane selectivity for monovalent ions [T.K. Sata, 1972]. Tokuyama Soda has commercialized monovalent cation selective membranes (Neosepta® CMS) prepared by forming a thin polyelectrolyte layer on the surface [T.K. Sata, 1986]. The permeability ratio of sodium to calcium is more than 20 for such a membrane.

Monovalent anion selective membranes have been developed mainly to prevent the permeation of sulfate which can cause scaling due to the precipitation of calcium sulfate in desalination of brackish water by electrodialysis. The permselectivity of anion-exchange membranes for monovalent anions can be increased by the formation of a highly cross-linked layer of the surface of an anion-exchange membrane [R. Yamane et al., 1964]. Also the formation of a negatively charged polyelectrolyte layer on the surface of an anion-exchange membrane increases its permselectivity for monovalent ions [K. Mihara et al., 1973]. The hydrophilicity of anion-exchange groups in the membrane also effects the permselectivity for specific anions. More hydrophobic anion-exchange groups have a higher permselectivity for less hydrated ions and vice versa [T.K. Sata et al., 1995]. Based on this concept membranes with high selectivity for nitrate and bromide over chloride have been developed. There are more preparation techniques to increase the permselectivity of anion-exchange membranes for certain anions described in the literature [T.K. Sata et al., 1997]. A monovalent anion selective membrane which shows a permeability ratio of sulfate to chloride of about 0.01 is the Neosepta® ACS which has a thin, highly cross-linked layer on the membrane surface.

2.3.2 Proton Permselective Cation-Exchange Membranes

Generally the permeation of protons is significantly higher, i.e. 4 to 5 times, than that of other cations. However, for certain applications such as the recovery of acids from a mixture with salts it is desirable to have a cation-exchange membrane with very high proton selectivity. Today two types of cation-exchange membranes with these properties are available. One is an amphoteric type ion-exchange membrane in which sulfonic acid and ammonium groups exist at a certain ratio [R. Yamane et al., 1965]. The second type is a cation-exchange membrane having a thin positively charged layer on the surface [T.K. Sata et al., 1979]. Both membranes show a proton permeability of more than 40 times that of sodium.

2.3.3 Anion-Exchange Membranes of High Proton Retention

Generally protons easily permeate through a conventional anion-exchange membrane because of the different transport mechanism of protons in an aqueous environment. Thus, it is difficult to obtain high acid concentrations in the electrodialysis of acid solutions or in the electrodialytic production of acids and bases with bipolar membranes without a significant loss in current utilization due to proton leakage through the anion-exchange membranes. Thus, a substantial effort has been concentrated on the development of anion-exchange membranes with decreased proton leakage. To reduce the proton permeability of anion-exchange membranes the fixed charge density of the membrane should be as high as possible. Furthermore, membranes containing weakly dissociated anion-exchange groups that are less hydrated also reduce the proton permeability [G. Pourcelly et al., 1994]. Commercially available membranes with improved proton retention contain 4-vinylpyridine as a key component. Thin layers of polypyrrole on conventional anion-exchange membranes show a remarkable decrease in proton permeability. The membranes are prepared by equilibrating a conventional anion-exchange membrane with an aqueous pyrrole solution. The membrane is then immersed in a ferric chloride solution to polymerize the pyrrole adsorbed by the membrane. The electrical resistance of the membrane hardly increases in spite of the decreased proton permeability because the polypyrrole layer at the surface of the anion-exchange membrane is extremely thin [T.K. Sata et al., 1993]. The Neosepta® ACM resembles this type of membrane. It exhibits low proton permeability and enables an efficient acid concentration.

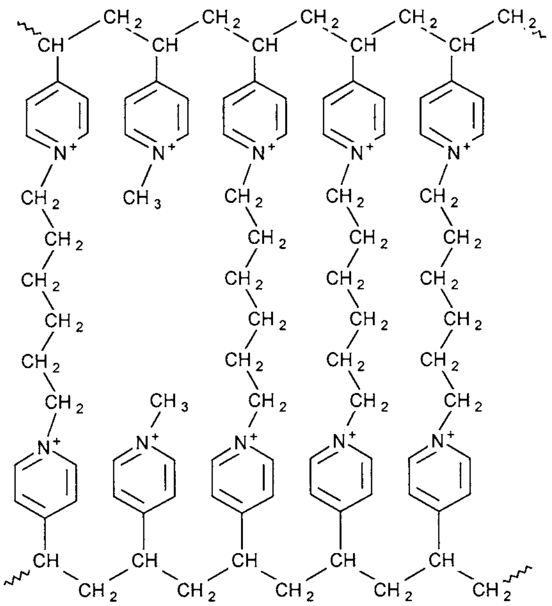
2.3.4 Anti-Fouling Anion-Exchange Membranes

Fouling of membranes is a common problem in all membrane separation processes. Ion-exchange membranes are fouled by ionic components of medium molecular weight such as ionic surface active agents or proteins having charges opposite to the fixed charges of the membrane. Generally, the anion-exchange membrane is more sensitive to fouling than cation-exchange membranes [E. Korngold, 1970]. However, significant improvements have been made in the development of anion-exchange membranes with low fouling tendencies. Fouling of anion-exchange membranes often occurs when the anion is small enough to penetrate into the membrane structure, but its electro-mobility is so poor that the membrane is virtually blocked. To overcome this problem, different companies developed membranes, such as the Neosepta® AMX which is characterized by a high permeability for large organic anions. In general, the permselectivity of these membranes is lower than that of regular membranes. Since the pore diameter of ion-exchange membranes is in the range of 1 nm, polyelectrolytes of high molecular weight, i.e. molecular weights > 1000 Dalton are not harmful to ion-exchange membranes. However, ionic compounds with molecular weight of several hundred Dalton can cause membrane fouling. According to some earlier studies concerning the permeability of commercial anion-exchange membranes, the upper molecular weight limit for practical electrodialytical separations is in the range of 150 Dalton [H. Itoh et al., 1986], [R. Dohno et al., 1975]. For instance, a molecular weight of 350 Dalton is to be considered as a maximum size for any charged component to effectively being transported through the Ionac MA-3475 membrane.

Ionics Inc. produces a macroreticular membrane which is less sensitive to traces of detergents [R.B. Hodgdon et al., 1973]. It is produced by dissolving an organic compound in the membrane forming system. When the material diffuses from the membrane after the polymerization, large pores are left behind. Alternatively, certain salts such as potassium iodide are added to the solvent of the binder polymer, which mostly is dimethylformamide. Through these pores, large anionic molecules can penetrate, thus preventing a steep increase in the electrical resistance.

Another type of anti-fouling anion-exchange membrane is produced by Tokuyama Soda. The membrane is coated with a thin layer of cation-exchange groups causing electrostatic repulsion of organic molecules. In practice the coating is done by weak sulfonation of the membrane surface, followed by the ordinary chloromethylation and quaternization steps.

One method to improve the permeability of anion-exchange membranes for organic acids having molecular weights in excess of 300 Dalton is based on the adjustment of the degree of cross-linkage and the chain length of the cross-linker in the polymer network, as indicated by the following structure [W.G. Gudernatsch et al.,1990]:

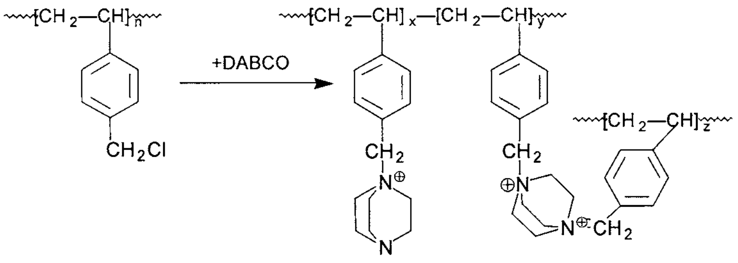


During the membrane formation, poly-4-vinylpyridine is quaternized with methyliodide and simultaneously cross-linked together with different dibromoalkanes.

Ion-exchange membranes based on aliphatic polymers show reduced organic fouling in natural waters when compared to membranes based on aromatic polymers [R.B. Hodgdon, 1992] . The membranes prepared from aliphatic polymers also allow operations with solutions containing 0.5 ppm chlorine and for shock chlorination up to 20 ppm free chlorine.

2.3.5 *Alkaline Stable Anion-Exchange Membranes*

In several technical interesting applications, the economics of the process are affected by the limited stability of currently available anion-exchange membranes in strong alkaline solutions. In the case of cation-exchange membranes the chemical stability could be improved by perfluorination of the polymer backbone, resulting in membranes such as the Nafion® or Flemion®. Comparable attempts with anion-exchange membranes to overcome the poor alkaline stability have so far failed. Since the fluorcarbon-type anion-exchange membranes cannot overcome the problem of instability under strong basic conditions, it is assume that the alkaline stability of an anion-exchange membrane is determined by the stability of the positively charged groups. By determining the disintegration rate of quaternized amines in alkaline solutions an anion-exchange membrane with considerable improved alkaline stability was developed [B. Bauer et al., 1990]. It was shown, that due to their higher acidity the cross-linked bis-quaternary structures have a much higher alkaline stability than the mono-quaternary ammonium groups. The highest alkaline stability was obtained with 4-diazabicyclo-[2.2.2]-octane (DABCO). Chloromethylated polystyrene can react with DABCO according to the following scheme:



An equimolar ratio of chloromethyl groups to the DABCO yields a membrane which is not cross-linked. By reducing the ratio of the chloromethyl groups to the DABCO monomer to >1 the membrane is partially cross-linked. The cross-linking reduces the swelling of the membrane drastically and increases its chemical and mechanical stability but it also increases the electrical resistance significantly. This is due to the fact that the bis-quaternary DABCO structure converts the positive charges into a piperazine system. However, the chemical stability of the membrane is not effected.

Instead of polystyrene other chloromethylated polymers such as polysulfone or polyethersulfone can be used.

2.3.6 Bipolar Membranes

Bipolar membranes have recently gained increasing attention as an efficient tool for the production of acids and bases from their corresponding salts by electrically enforced accelerated water dissociation. The process which has been known for many years is economically very attractive and has a multitude of interesting technical applications [K.J. Liu et al., 1977]. So far, however, large-scale technical use of bipolar membranes has been rather limited by the availability of efficient membranes.

The principal structure of a bipolar membrane and its function is illustrated in Figure 3.3.

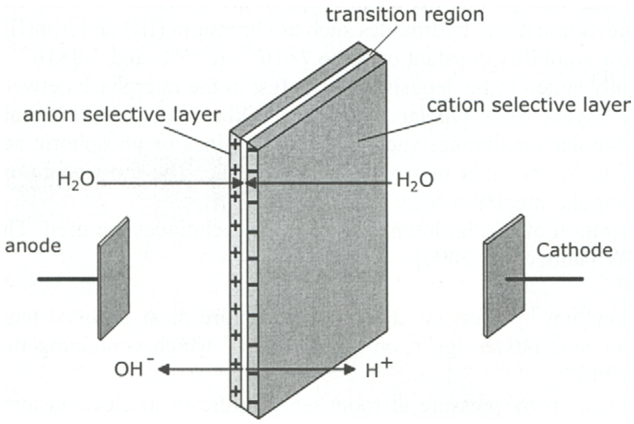


Fig. 3.3 Schematic drawing illustrating the structure of a bipolar membrane.

This figure shows an anion- and a cation-exchange membrane arranged in parallel between two electrodes similar to conventional electrodialysis. If there are no salt ions in the transition region between the two membranes and an electrical potential gradient is applied the transport of the electrical charges through the membranes is accomplished exclusively by protons and hydroxyl ions which are available even in pure water in a concentration of 10^{-7} mole per liter due to the dissociation equilibrium of water. Thus, an alkaline solution is formed on the anion-exchange side and an acid solution on the cation-exchange side of the bipolar membrane. The dissociated water which is transferred from the bipolar membrane to the outside phases as protons and hydroxide ions are continuously replenished from the outer phases by diffusion.

The most important properties of bipolar membranes are:

- low electric resistance,
- high selectivity for the counter-ions, i.e. complete exclusion of co-ions,
- excellent stability in solution with extremely low and high pH-values,
- high water dissociation capability,
- high water permeability of the monopolar layers.

Low electrical resistance, high permselectivity, and good chemical stability are properties required in all ion-exchange membranes. In addition bipolar membranes must be able to split water into protons and hydroxyl ions at a very fast rate[K.N. Mani, 1991]. The mechanism of water dissociation in bipolar membranes will be discussed later. Although the actual mechanism of water dissociation in the bipolar membrane is still subject of a rather controversial discussion it is generally assumed that the water dissociation in bipolar membranes is based on a proton transfer reaction that is catalyzed by weak acids and bases. It is assumed that the best catalytic effect can be achieved if the pK_a- or pK_b-value of the interphase material is close to 7 [H.J. Rapp, 1995]. Some weak ion-exchange groups such as tertiary amines, phosphoric acid, carboxylic acids or pyridine show the required pK_a-values. Certain heavy metal ion complexes, such as chromium(III)- or iron(III)-complexes provide the required catalytic water dissociation effect. In principle there are many more suitable metal ions available. But there is an additional requirement for the catalytic material to be effective for a long term period, i.e. it must stay in the interphase for the anticipated lifetime of the membrane. Some metal hydroxides such as chromium (III) and iron(III) hydroxide have an extremely low solubility constant of $K= 6.7\times10^{-31}$ at 25°C and $3{,}8\times10^{-31}$ at 18°C and they are thus especially suited to be deposited as catalyst in the interphase between the cation- and anion-exchange layers of a bipolar membrane. Other catalytic components used in the preparation of bipolar membranes such as tertiary amines or phosphoric acids are generally directly bonded to the polymer matrix of the membrane. The most commonly used catalytic components in bipolar membranes are listed in Table 3.1.

For the preparation of bipolar membranes several techniques are used. The most important ones are [F.G. Wilhelm et al., 2000]:

- The lamination by pressure at room temperature or at elevated temperature of solid cation- or anion-exchange resin sheets one of which containing the catalytic active component.
- The lamination by pressure at room temperature or at elevated temperature of solid cation- or anion-exchange resin sheets with an intermediate layer containing the catalytic active material.

- Casting a film from a solution containing an anion-exchange resin with the catalytic active component on a solid sheet of the cation-exchange resin.
- Casting a film from a solution containing a cation-exchange resin with the catalytic active component on a solid sheet of the anion-exchange resin.
- Co-extrusion of a cation- and anion-exchange resin one of which is containing the catalytically active component.

There are certainly many more techniques for the preparation of bipolar membranes described in the literature. However, very few are utilized commercially.

Table 3.1 Components used as catalytic material for the preparation of bipolar membranes.

material	form of application	pK_a-value	reference
$Cr(OH)_3$	as salt in the cation-exchange layer or the interphase		R. Simons, 1993
$Fe(OH)_3$	as salt in the cation-exchange layer or the interphase		F. Hanada et al., 1991
$-NR_2$	bond to the matrix of the anion-exchange membrane	~ 9	B. Bauer et al., 1988
$R-PO_3H$	bond to the matrix of the cation-exchange membrane	~7	N.V. Sheldeshov et al., 1986

The first bipolar membranes were prepared by simply laminating conventional cation- and anion-exchange membranes back to back. These membranes showed relatively high electric resistance. The high resistance of the membranes was caused by the interphase between the cation- and anion-exchange layers which contains only completely de-ionized water. To provide an area resistance which is in the same order of magnitude as that from the ion-exchange layers the interphase must be very thin, i.e. between 1 and 5 nm. Since the surface roughness of conventional ion-exchange membranes is in the order of several µm the contact between the laminated membranes is rather poor as indicated in Figure 3.4 which shows a schematic drawing of the a cross-section of two bipolar membranes.

The Figure 3.4 a) shows a cation-exchange and an anion-exchange resin layers which are in direct contact only at a limited number of points. In between these contact points there are areas where the distance between the two layers is comparatively large. Since the gap in these areas is filled with pure water its electric resistance is very high. The current through such a bipolar membrane passes mainly through contact points where very high current densities are obtained which often result in so-called "hot spots" where very high temperatures can be reached leading to a destruction of the membrane. If bipolar membranes are prepared by simply laminating conventional cation- and anion-exchange membranes back to back more satisfactory properties can be obtained by introducing a special surface treatment [R. Simons, 1986, 1993] or by introducing a thin layer containing the catalytically active groups [B. Bauer, 1993]. The electrical resistance of a bipolar membrane depends to a very large extent on the resistance of the area between the two ion-exchange membranes.

Membranes with a more uniform and thin interphase are obtained when a cation- or anion-exchange resin is cast on a solid film carrying the opposite charge [F.P. Chlanda et al., 1976], [R.B. Hodgdon, et al., 1989]. Even when the solid film has a certain surface roughness there will be a close and uniform contact over the entire surface as indicated in Figure 3.4 b).

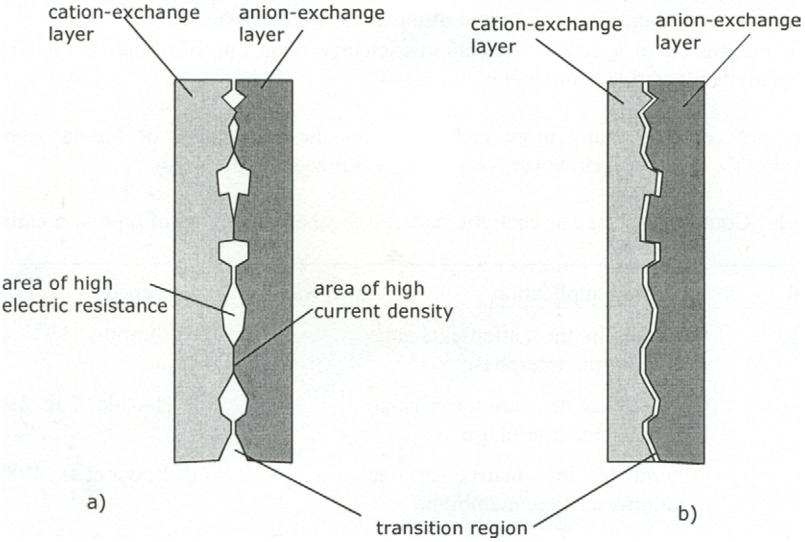
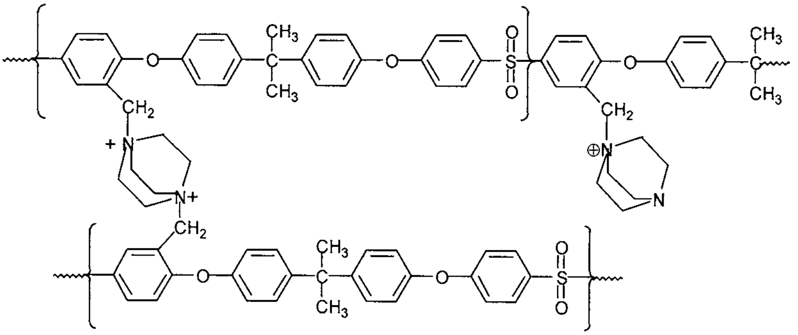


Fig. 3.4 Schematic diagram illustrating the transition region in a bipolar membrane prepared a) by laminating two conventional ion-exchange membranes back to back by pressing and b) by casting liquid anion-exchange resin on a solid ion-exchange membrane.

Today, most bipolar membranes are composed of a three layer structure, i.e. a cation-exchange layer, an anion-exchange layer and an intermediate layer containing a weak acid or base catalyst. This intermediate layer is a transition region between the two ion-exchange membranes where the water dissociation takes place. To have the required water dissociation capability it must contain the appropriate concentration of catalytic components. It must also be very thin to exhibit acceptable ion conductivity. Weakly dissociated ionic groups such as tertiary amines or certain metal hydroxides fulfill the requirements for catalytic components. However, their specific electrical resistance is relatively high. To minimize the electrical area resistance the thickness of the interphase or transition region between the oppositely charged layers should be as thin as possible, preferably less than 5 nm. In some commercial bipolar membranes heavy metal hydroxides are deposited in the interphase to catalyze the water dissociation [F. Hanada et al., 1993]. Tertiary ammonium groups as fixed charges at the surface of an anion-exchange membrane have the same effect and are therefore also used [B. Bauer et al., 1988].

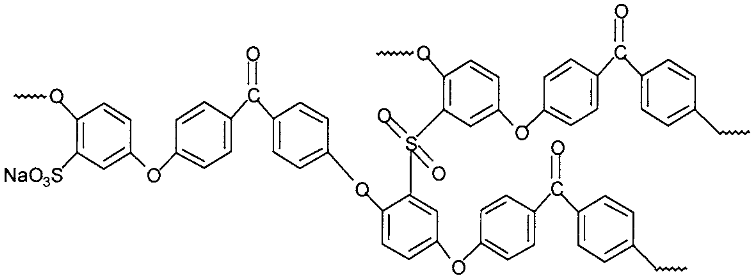
A bipolar membrane with satisfactory properties, i.e. low electrical resistance at high current density, high water dissociation rates, low coion transport rate, high ionselectivities, good chemical and thermal stability in strong acids and bases can be prepared, e.g. as a laminate of anion- and cation-exchange layers.

An anion-selective layer with the required properties can be obtained by reaction of chloromethylated polysulfone dissolved in N-methyl-2- pyrrolidone with the mono-quaternary salt of 4,4'-diazabicyclo-[2.2.2]-octane (DABCO) to the following structure [H. Strathmann et al., 1993].



The cross-linking density can be adjusted by the ratio of DABCO to the chloromethylated polysulfone. The morphology of the anion-exchange layer is of a homogeneous type structure.

The cation-selective layer can be prepared by introducing sulfonic acid groups as fixed charges into a polyetheretherketone matrix using chlorosulfonic acid. The coion transport and the swelling behavior can be decreased by partial cross-linking which is done during the membrane formation step as indicated in the following scheme:



The above described bipolar membrane is composed of:

- a highly permselective anion-exchange layer which shows excellent alkaline stability,
- an equally highly permselective cation-exchange layer which exhibits excellent acid stability, and
- a transition region with a limited number of catalytically active tertiary ammonium groups.

This bipolar membrane shows most of the properties requested in practical applications where the cation-selective layer of the bipolar membrane is generally in contact with an acid solution and should thus be stable in strong acids. The anion-exchange layer is in contact with an alkaline solution and should thus be stable in strong bases.

The electrochemical properties of the ion-exchange layers prepared by the above described procedures are listed in Table 3.2. Properties of commercial bipolar membrane do not vary significantly from the data given in the table [R.B. Hogdon et al. 1989], [R. Simon, 1986, 1993], [F. Hanada et al., 1993]. However, there are also single sheet membranes prepared by plasma induced polymer grafting [Y. Yokoyama et al., 1989], [H. Hurwitz et al.,1998].

Table 3.2 Electrochemical properties of the cation- and anion-selective layers of a bipolar membrane prepared by the above described technique

membrane properties	anion-exchange layer	cation-exchange layer
ion-exchange capacity [meq g^{-1}]	1.2	1
membrane thickness [μm]	60	60
area resistance [Ωcm^2]	1.05	1.31
permselectivity [%]	97.5	98.5
swelling [%]	8	12.5

2.3.7 Ion-Exchange Membranes for Diffusion Dialysis

Since anion-exchange membranes are in general quite permeable for protons acids can be recovered from a mixture with salts by diffusion dialysis. The principle of the process was described earlier. The driving force for the transport of protons is the concentration of the acid in a feed solution and a stripping solution. For economical reasons high acid recovery rates are required. Thus, the concentration difference between the stripping and the feed solution is relatively small and the transport rates are low. To obtain acceptable fluxes the anion-exchange membranes should be as thin as possible and have very low salt ion leakage. Thin and mechanically strong anion-exchange membranes are difficult to prepare from copolymers cross-linked by divinylbenzene. Thin anion-exchange membranes with satisfactory mechanical strength and high proton fluxes can be prepared from block type aromatic condensation polymers.

Accordingly, hydroxide ions easily permeate through cation-exchange membranes. Thus, bases such as sodium hydroxide can be recovered from a mixture with salts by diffusion dialysis. The cation-exchange membranes developed for this process are relatively thin and they are stable in a strong alkaline environment. The main application of diffusion dialysis is the recovery of sodium hydroxide from aluminum etching baths. Since the aluminate ion is relatively bulky, leakage through the membrane is relatively small even in a loosely structured anion-exchange membrane.

There are many more special property membranes developed with a very specific application in mind.

2.3.8 Other Special Property Ion-Exchange Membranes

Large effort is concentrated to develop ion-exchange membranes as separators for fuel cells and especially the methanol direct conversion fuel cell [J. Kerres, 2000]. In addition to low electrical resistance membranes used in fuel cells must have good chemical stability at elevated temperatures up to 150°C and well controlled water and eventual methanol permeability. Today mainly fluorocarbon cation-exchange membranes of the Nafion® or Flemion® type are used. But new structures with better temperature stability and lower methanol leakage are under development [J. Kerres et al., 2001]. Also, certain electro-organic syntheses require special property membranes with satisfactory electrical properties and good chemical stability in the reaction environment.

Mosaic membranes which are composed of macroscopic domains of cation- and anion-exchange resins separated by a neutral polymer were developed for the concentration of salt solutions by a process referred to as piezodialysis. In this process a hydrostatic pressure is applied to transport salt solutions through a mosaic membrane. Since both cations and anions are simultaneously adsorbed by the cation- and anion-exchange domains of the membrane an electric circuit is formed which allows the salt to pass the membrane. As long as the fixed charge density of the membrane is higher than the ion concentration in the feed solution salt will preferentially permeate the membrane under a hydrostatic pressure driving force and will thus be concentrated in the permeate. Mosaic membranes can be prepared by distributing cation- and anion-exchange particles of sub-micron size in a neutral hydrophilic polymer film. Alternatively, mosaic membranes can be prepared by a film casting method using a block polymer composed of a part in which cation-exchange groups and a part where anion-exchange groups can be introduced [Y. Miyamoto et al., 1991]. However, today mosaic membranes seem to be of little technical and commercial relevance.

3 CHARACTERIZATION OF ION-EXCHANGE MEMBRANES

Characterization of ion-exchange membranes is closely related to their preparation. The most interesting properties of ion-exchange membranes are [K.S. Spiegler, 1958]:

- the electrical resistance in different electrolyte solutions,
- the type and density of fixed charges and their distribution in the membrane matrix,
- the permselectivity of the membrane for different ions of the opposite and same polarity,
- the transport rate of neutral components, especially water, under operating conditions, i. e. under an applied current,
- the mechanical stability at ambient and elevated temperatures and the swelling behavior in different electrolyte solutions,
- the chemical stability in the presence of oxidizing agents and at extreme pH-values.

A series of procedures and techniques are applied to determine the different membrane properties. Microscopic examination yields information on heterogeneity of the membrane structure and in case of reinforced membranes the type of reinforcement used. The electrical charge of an ion-exchange membrane can be determined qualitatively by using indicator solutions. A drop of a 0.05% solution of methyleneblue and methylorange on a membrane sample stains a yellow spot on top of an anion-exchange membrane and a deep blue spot on top of a cation-exchange membrane, respectively. For a quantitative characterization more complex procedures are applied such as the determination of the ion-exchange capacity of the membrane, its electrical resistance and the membrane transport properties for different ions and neutral components under various conditions which are close to the operating conditions in a specific application. Additional information can be obtained by impedance spectroscopy and transition time measurements as well as from the determination of osmotic and electro-osmotic water transfer. Bipolar membranes are further characterized in terms of the water dissociation capability and salt leakage under operating conditions [H. Strathmann, 1995].

3.1 The Structure of Ion-Exchange Membranes and its Characterization

The properties of ion-exchange membranes are closely related to their structures on a microscopic scale. Most hydrocarbon polymer membranes have a rather regular distribution of cross-linkings and ionic groups attached to a back bone of aromatic rings. As a result these membranes are quite homogeneous in their structure even on a microscopic scale. Membranes based on linear fluorocarbon polymers have a backbone of a highly crystallized polymer with ionic groups fixed on a side chain. These membranes are quite heterogeneous on a microscopic scale with distinct crystalline areas formed by the linear fluorocarbon polymer and separated by amorphous, highly hydrophilic domains formed by the side chains with the ionic groups. The structure of the fluorocarbon polymers based membrane have been studied in great detail using transmission electron microscopy, wide and small angle X-ray diffraction [T.H. Gierke et al., 1982], differential scanning calorimetry, infrared and nuclear magnetic resonance spectroscopy [M. Falk, 1982] and [R.A. Komoroski et al., 1982]. From the experimental evidence it can be concluded that the fluorocarbon polymer membranes have a heterogeneous two phase structure composed of crystalline polytetrafluorethylene and amorphous vinylether with fixed charges as depicted in Figure 3.5.

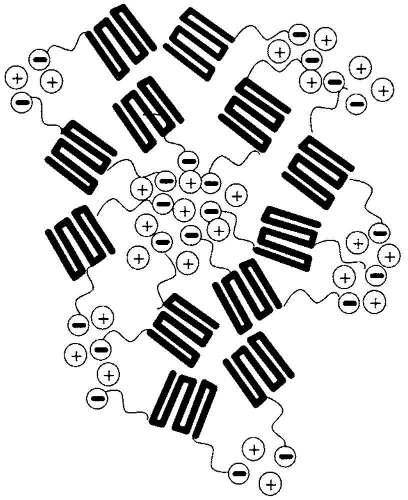


Fig. 3.5 Schematic drawing illustrating the structure of the fluorocarbon polymers based membranes showing the crystalline polytetrafluorethylene region and the negatively fixed charges on the vinylether linkages.

The amorphous region containing a cluster of fixed charges, counterions, and water is extremely hydrophilic and swells in water or aqueous solutions while the crystalline region acts as cross-linkage and restricts the swelling of the membrane. In the literature the hydrophilic clusters are pictured as spherical regions with a diameter of ca. 4 to 6 nm connected by “bottle necks” between crystalline regions of ca. 1 nm in diameter as depicted in Figure 3.6. The mobility of the counter-ions within the hydrophilic cluster is very high. The transport of the counter-ions from one cluster to the next, however, is restricted by the “bottle neck". The size of the hydrophilic cluster is a function of the swelling of the membrane and depends on the concentration of the electrolyte solution in equilibrium with the membrane.

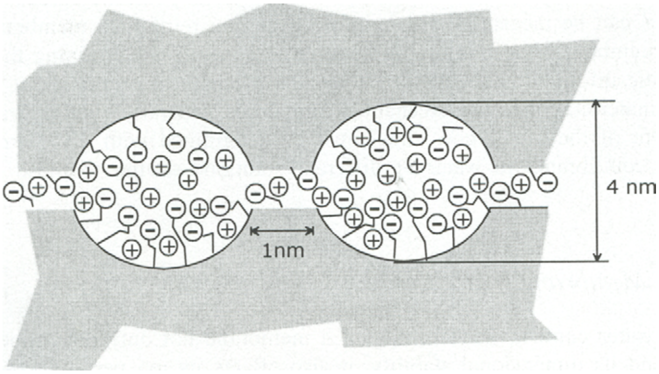


Fig. 3.6 Schematic picture illustrating the cluster network of a fluorocarbon polymer based ion-exchange membrane.

3.2 Mechanical Stability, Swelling, and Permeability of Membranes

A detailed mechanical characterization of ion-exchange membranes involves the determination of thickness, swelling, and dimensional stability in water or different test solutions, tensile strength and hydraulic permeability measurements. All mechanical characterization tests should be carried out with pretreated and well equilibrated membranes in a controlled environment. Relevant information related to the storage and handling requirements of the membranes is obtained from the determination of the dimensional changes between wet and dry states of the membrane and by tensile strength measurements. The tensile strength and information concerning the plastic or elastic deformation of a membrane is obtained from a stress versus strain diagram as shown schematically in Figure 3.7.

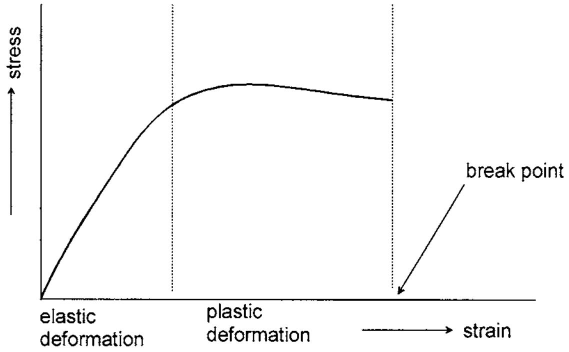


Fig. 3.7 Stress versus strain diagram of an ion-exchange membrane sample indicating the elastic and plastic deformation and the breakpoint.

The strain versus stress curves of ion-exchange membranes generally show three distinct areas. At relatively low strain the membranes show elastic deformation, with increasing strain the membranes show plastic deformation, and at a certain point they break. The strain versus stress curves can be measured with reinforced or non reinforced membranes. However, in reinforced membranes the reinforcing material is generally determining the tensile strength and very little information is obtained about the mechanical properties of the ion-exchange membrane material. Since the mechanical properties generally change drastically with the water content of the membranes they must be determined with dry membranes and with membranes equilibrated in water or different solutions similar to those used in practical applications.

3.2.1 The Membrane Water Content

The gel water content, i.e. swelling of a membrane not only determines its mechanical properties and its dimensional stability, it also effects its ion permselectivity, its electrical resistance, and its hydraulic permeability.

The swelling of a membrane depends on a number of different parameters such as the nature of the basic membrane polymer, the nature of the ion-exchange groups and their concentration in the membrane, the counter ions, the cross-linking density and the homogeneity of the membrane. The water content of an ion-exchange membrane depends not only on the properties of the membrane but also on the composition of the solution with which the membrane is in contact. Especially the concentration of the solution has a significant effect on the water content of the membrane because of osmotic effects that are directly related to the chemical potential difference of the water in the membrane and in the solution as has been shown earlier in the discussion of the electrochemical and chemical equilibrium of a membrane with its surrounding. The state of the water in the membrane can also be rather different. Part of the water is so-called "free" water. Another part of the water is strongly bound within the hydration shell of the counterions and the fixed charges of the membrane, while again another part is more loosely bound to the basic polymer matrix. The different water structures in ion-exchange membranes is extensively studied applying differential scanning calorimetry, infrared spectroscopy, and nuclear magnetic resonance. Most of these studies are carried out on perfluorinated ionomer membranes [M. Escoubes et al., 1982], [M. Falk, 1982], and [R.A. Komoroski et al., 1982]. These membranes are rather heterogeneous in structure with distinct, highly hydrophobic crystalline domains and pores filled with the electrolyte solution while apparently the water in these membranes shows very different structures. In sulfonated polystyrene or polysulfone the absorbed water is more homogeneously distributed in the membrane matrix and more homogeneous in its structure.

Studies of the water structure within the membrane and its interaction with the membrane polymer, fixed charges, and counter-ions require more sophisticated spectroscopic measurements. The total water uptake of the membrane in equilibrium with an electrolyte solution can be determined by measuring the weight difference between a membrane in the wet and dry state. To determine the water content of a membrane, a sample is equilibrated in deionized water or any other test solution. After removing the surface water from the sample, the wet weight of the swollen membrane is determined. The sample is then dried at elevated temperature over phosphorous pentoxide under reduced pressure until a constant weight is obtained. The water content of a membrane is obtained in weight percent by:

$$\text{wt\% swelling} = \frac{W_{wet} - W_{dry}}{W_{wet}} \times 100 \qquad (3.1)$$

Here W_{wet} and W_{dry} are the weight of a membrane sample in the wet and the dry state.

Determining the membrane water sorption by mass balance seems quite simple. However, some precautions must be taken to achieve satisfactory measurement accuracy. For example, surface water on a wet membrane must be removed without loss of water from the membrane bulk phase. This can be difficult with very thin membranes. During the drying procedure all water must be removed. This often requires drying for an extended time period at elevated temperature in vacuum which may lead to some irreversible structural changes of the membrane. In comparing commercial membranes from literature references it is mandatory to know the exact experimental procedure used in determining the membrane water sorption. The equilibrium water sorption of various commercial ion-exchange membranes are listed in Table 3.3.

Table 3.3 Water sorption of various commercial membranes in equilibrium with NaCl- solutions of different concentrations

membrane	solution [NaCl mol/L]	water sorption [g H_2O/ g dry membrane]	water sorption [mol /fixed ions]	reference
Nafion 117 1)	0.2	0.14	11.9	H.L. Yaeger, 1982
Flemion AR 1.25 2)	1.0	0.23	10.6	M. Tasaka, 1992
Neosepta CL 25T 2)	0.5	0.34	10.5	T. Sata, 1986
Neosepta C 66 5T 2)	0.5	0.42	9.5	T. Sata, 1986
Neosepta AM 1 2)	0.5	0.30	8.3	T. A. Davis, 1997
Neosepta ANR 1 2)	0.5	0.23	6.1	T. A. Davis, 1997
Ionics CR 67 3)	1.0	0.46	11.7	Ionics brochure

1) produced by Dupont, 2) produced by Tokuyama, 3) produced by Ionics

The fixed charges of the membranes listed in Table 3.3 are strong acidic ($-SO_3^-$-groups) in the cation-exchange membranes and strong basic ($-NR_3^+$-groups) in the anion-exchange membranes. Membranes containing weak acidic or weak basic groups generally show significantly lower water sorption. The water sorption of perfluorinated ion-exchange membranes with carboxyl groups as fixed charges is about half of that of membranes with sulfonic acid groups.

The water sorption depends also on the type and concentration of the counterions and is generally decreasing with the size of the hydrated counterion. Thus, for a cation-exchange membrane the water sorption is decreasing along the series $Li^+ > Na^+ > K^+ > Mg^{++} > Ca^{++}$.

3.2.2 Hydraulic Permeability of Ion-Exchange Membranes

Hydraulic permeability measurements provide information on the diffusive or convective transport of components through a membrane under a hydrostatic pressure driving force. In most practical applications of electrodialysis and related processes the hydraulic permeability plays a minor role for the overall performance of the membrane in a given application since the processes are generally operated without pressure gradients across the membrane. However, for the determination of pinholes in ion-exchange membranes which will not only obscure the membrane permeability for different components but will also invalidate most applications where hydrostatic pressure differences across the membrane are obtained hydraulic permeability tests are important as a quality control step. Larger pinholes can also be detected quickly by placing a wet membrane sheet on a sheet of white absorbent paper. Then a 0.2% solution of methylene blue for an anion-exchange membrane or a 0.2% solution of erythrocein-B for a cation-exchange membrane is spread over the entire surface of the membrane. If no spots of the dye can be observed on the paper, the membrane is free of large pinholes. The hydraulic permeability of the membrane is determined at room temperature using deionized water and a hydrostatic pressure driving force in a conventional filtration cell as used in reverse osmosis or ultrafitration experiments. The permeability can then be calculated from the volumetric flow rate.

3.2.3 Long-Term Chemical Stability of Membranes

The economics of processes using ion-exchange membranes in different applications is determined to a large extent by the chemical stability of the membranes under process conditions. The structure, the mechanical and electrochemical properties of ion-exchange membranes can be effected by oxidizing agents, high or low pH-values, extreme temperatures, loss of water, etc.. The structure and the mechanical properties of the membranes can be effected by degradation of the basic polymer or re-crystallization and aging due to loss of water or plasticizing agents. The deterioration of the electrical chemical properties can be caused by the loss of fixed charges due to the splitting-off functional ion-exchange groups. Also changes in the membrane structure and the irreversible loss of water effect the membrane ion transport properties and selectivity. Generally, the changes in membrane properties are time and temperature dependent. Reliable information about the long term stability of the membranes is of great importance for a process design and cost calculation. For a fast evaluation membrane samples are exposed to oxidizing agents or acids and bases and other chemical components in much higher concentration and at higher temperature than expected in practical use. Structural mechanical changes are determined by visual or microscopic investigation and standard mechanical and electrochemical tests comparing exposed membrane samples with new unexposed samples. Since the useful life of membranes under process conditions should be as long as possible and is generally in the range of a couple of years membrane stability tests are very time consuming. However, some information concerning chemical and mechanical stability under operating condition may be obtained in short term tests carried out at elevated temperatures that are well above the anticipated operating temperature. Nevertheless, in many cases long-term pilot plant tests are mandatory to get a reliable estimation of the life of the membranes in practical applications.

3.3 Determination of Electrochemical Properties of Membranes

The performance of ion-exchange membranes in the various electromembrane processes is determined to a very large extent by their electrochemical properties. Therefore, a major task in characterizing ion-exchange membranes is the determination of their electrochemical properties such as the fixed charge density, the electrical resistance, the ion permselectivity, and the transport of non-ionic components such as water or of other neutral molecules.

3.3.1 The Ion-Exchange Capacity of a Membrane

The ion-exchange capacity of charged membranes is a crucial parameter which effects almost all other membrane properties. Its determination is therefore an important step in characterizing an ion-exchange membrane. The ion-exchange capacity is a measure of the number of fixed charges per unit weight of dry polymer. It is usually expressed in milli-moles per gram which in almost all ion-exchange membranes is identical with milli-equivalents per gram dry membrane since in ion-exchange membranes the fixed charges are mono-valent. Experimentally the ion-exchange capacity of a membrane is readily determined by titration of the fixed ions with 1N NaOH or HCl, respectively. For these tests, cation- and anion-exchange membranes are equilibrated for about 24 h in 1N HCl or 1N NaOH, respectively, and then rinsed free from chloride or sodium for 24 h with deionized water. The ion-exchange capacity of the samples is then determined by back titration with 1N NaOH or 1N HCl, respectively. Weak base anion-exchange membranes are characterized by equilibration in 1N sodium chloride and titration with standardized 0.1 N silver nitrate solution. The samples are then dried, and the ion-exchange capacity is calculated for the dry membrane. The accuracy of the measurement depends on the complete exchange of ions in the membrane which can take some time. In most commercial membranes complete ion-exchange is achieved within a couple of minutes. The concentration of the fixed ion in commercial membranes is in the range between 1 and 3 milli-equivalent per gram. The experimentally measured ion-exchange capacity of a membrane is an average value assuming that the ions are homogeneously distributed over the entire polymer matrix. In many membranes such as most of the perfluorenated cation-exchange membranes the fixed ions are clustered and the local fixed ion concentration may be significantly higher than the average value.

3.3.2 Electrical Resistance of Ion-Exchange Membranes

The electrical resistance of ion-exchange membranes is one of the factors which determine the energy requirements of electrodialysis processes. However, in most practical cases the membrane resistance is considerably lower than the resistance of the dilute solutions, since the ion concentration in the membrane is relatively high. The specific membrane resistance is usually reported as Ω cm or Ω m. From the engineering point of view, the membrane area resistance in units of $\Omega\ cm^2$ or $\Omega\ m^2$ is more useful and generally given in the literature describing commercial products. The electrical resistance of a membrane is determined by the ion-exchange capacity and the mobility of the ion within the membrane matrix. The ion mobility in the membrane depends strongly on the nature of the mobile ion species, i.e. its valence, its size, and its extent of hydration, and on the water content of the membrane. It is furthermore effected by the temperature and by the nature of the fixed ions, i.e. the interaction between the mobile ions with the fixed ions. The area resistance of ion-exchange membranes can be determined by direct current (DC) measurements or by alternating current (AC) measurements. In DC measurements the membrane is installed in a cell which consists of two chambers containing the test solution separated by the test membrane as indicated in Figure 3.8.

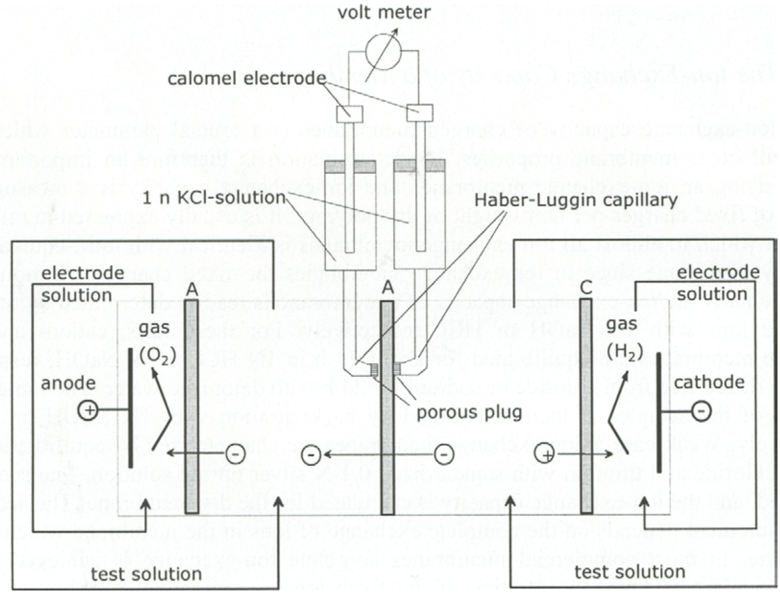


Fig. 3.8 Schematic drawing of a test cell for determining the resistance of ion-exchange membranes with direct current.

The two electrodes used to provide the electrical potential driving force to obtain a certain current are separated by membranes from the test solution to avoid gas bubbles to disturb the measurement. As test solution a 1 or 0.5 mol/L Na_2SO_4 solution is used. The same solution is also used to rinse the electrode chambers and remove the gases produced at the electrodes. The actual potential drop in DC measurements across the membrane is determined with calomel electrodes attached to Haber-Luggin capillaries placed with their tips close to the membrane surface. The potential drop between the Haber-Luggin capillaries is measured with and without the membrane in the test cell as a function of the current density passing through the cell. The resistance is given by the slope of the current versus the voltage drop curve. To obtain the membrane resistance the resistance of the cell without the membrane is subtracted from the resistance of the cell with the membrane.

The area resistance is given by:

$$r_{m+s} = R\,A_m = \frac{U}{i} \tag{3.2}$$

The membrane resistance is:

$$r_m = r_{m+s} - r_s \tag{3.3}$$

Here R is the resistance, A_m is the area of the membrane, U is the voltage drop measured between the Haber-Luggin capillaries and I is the current density, r_{m+s} and r_s are the area resistances of the cell with and without the membrane between the Haber-Luggin capillaries, and r_m is the area resistance of the membrane.

Typical test results obtained in a test cell of the above described design are shown in Figures 3.9 a) and b).

The experiments were carried out at 25 °C with a 1mol/L Na_2SO_4 test solution and a none reinforced prototype anion-exchange membrane based on functionalized polysulfone. Figure a) shows the test results obtained by measuring the area resistance between the Haber-Luggin capillaries with and without the test membrane as a function of the current density. Figure b) shows the area resistance of the membrane determined according to Equation 3.6.

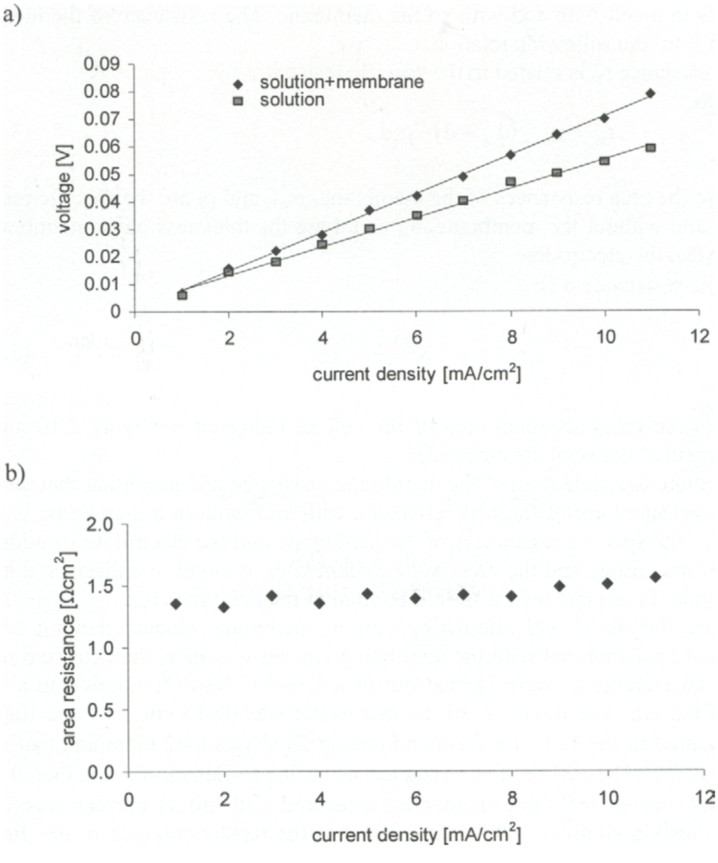


Fig. 3.9 Experimental results obtained with a prototype of non-reinforced anion-exchange membrane a) showing the voltage drop of the cell with a 1mol/L Na_2SO_4 solution at 25°C as function of the current density with a membrane and without a membrane, b) showing the area resistance as function of the current density calculated by Equation 3.3 from the experimental results.

The determination of the membrane resistance by direct current measurements is quite accurate as long as the position of the Haber-Luggin capillaries is as close as possible to the membrane and kept identical in the test with and without the membrane. To avoid boundary layer effects the bulk solution must be well mixed. But even if the boundary layer effects are well controlled the direct current measurements are always connected with a transport of ions resulting in a concentration change in the electrolyte solution at the membrane surface which can effect the accuracy of the measurement.

Concentration changes are avoided in resistance measurements with alternating current. Therefore, membranes have also been characterized in terms of their resistance by alternating current measurements. A typical test cell used for these tests is shown in Figure 3.10. Also in the case of alternating current the membrane resistance is determined from resistance measurements in a cell with and without the membrane. The resistance of the membrane can be calculated from the following relation:

The area resistance r_m is related to the specific resistance by:

$$r_m = \rho_{m+s}\left(d_m + d\right) - \rho_s d \tag{3.4}$$

Here r_m, are the area resistances of the membrane, ρ_{m+s} and ρ_s are the specific resistances of the cell with and without the membrane, d_m and d are the thickness of the membrane and the distance between the electrodes.

The specific resistance ρ is:

$$\rho = R\frac{A_m}{d} \tag{3.5}$$

Here A_m is the cross-sectional area of the cell as indicated in Figure 3.10 and R is the resistance measured between the electrodes.

For an accurate determination of the membrane resistance it is important that the difference between the measurement of the cell resistance with and without a membrane is as large as possible. Since the specific resistances of the membrane and the electrolyte solution are in the same order of magnitude and the membrane thickness d_m is small, the distance d has to be as small as possible. In reliable tests d should be smaller than 20 times d_m.

To compare the direct and alternating current membrane characterization a membrane which was first characterized with the alternating current was then characterized using direct current. The measurements were carried out in a 1 mol/L Na_2SO_4 solution in a cell with a distance d of 0.2 cm. The thickness of the membrane was 0.015 cm. The specific resistance that was measured in the cell with the membrane at 25°C was 6.62 Ωcm and that without the membrane was 5.75 Ω cm. The area resistance according to Equation 3.4 is then 0.273 Ωcm^2. The area resistance of the same membrane measured with direct current was 1.44 Ωcm^2. There is obviously a significant difference between the results obtained in the direct current and the results obtained in the alternating current membrane resistance measurements. The alternating current measurements give a much lower membrane resistance than the direct current measurements. This is a general finding. However, the magnitude of the difference in the results depends on the membrane structure. In very heterogeneous membranes the difference is larger than in more homogeneous membrane structures. The reason for the different results is that in direct current measurements the ions are physically transported through the membrane matrix, whereas in alternating current measurements the ions are only oscillating around their locations. Assuming the structure of an ion-exchange membrane consists on a microscopic scale of a solid neutral polymer phase and electrolyte filled pores, then the mobility of the ions in the pore liquid is high. But their transport through the membrane is hindered by the solid polymer structure which acts as a bottle neck between pores. This type of structure has been depicted in Figure 3.5 which shows a schematic drawing of a typical fluorocarbon membrane. In alternating current measurements the transport of the ions on a very small scale, i.e. in a pore is measured. In direct current measurements the transport of the ions is measured on a macroscopic scale which includes also the passage through a bottle neck between electrolyte filled pores. The direct current and alternating current difference is treated in detail in the literature [V.I. Zabolotsky et al., 1993].

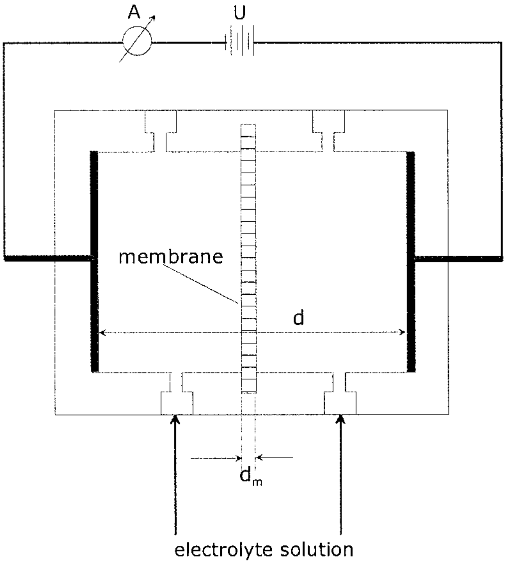


Fig. 3.10 Schematic drawing of a test cell used for membrane resistance measurements using alternating current.

In recent years, a rather elegant and reliable method of measuring resistances with alternating current is widely used. This method is based on impedance spectroscopy. The difference between the alternating current resistance measurements and the impedance spectroscopy is, that in the first case the frequency of the alternating current is kept constant while in impedance spectroscopy the frequency of the alternating current is changed and the response to the changing frequency is determined by a spectrometer.

Ion-exchange membranes display a variety of electrical properties that suggest that they can be modeled as a combination of electrical analog components. For example, an applied potential can produce a current flow through the membrane and this is indication that the membrane has a finite resistance. In addition, the charged groups at the membrane/solution interface provides sites for the redistribution of charges at the membrane surface when the transmembrane potential is changed. This charge redistribution is similar to that observed for a capacitor in which a potential change produces a change in the net charges. The electrolyte solutions and the electrodes on both sides of the membrane also have a certain resistance. The properties of the ion-exchange membrane, the solution, and the electrodes can be described electrically by an equivalent circuit as indicated in Figure 3.11, where C_m and R_m are the membrane capacitance and resistance, respectively, and R_s is the resistance of electrodes and the electrolyte solution.

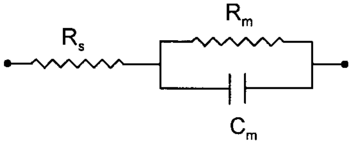


Fig. 3.11 Equivalent resistance-capacitance circuit for a simple membrane in an electrolyte solution neglecting electrode resistances and capacities.

To determine membrane resistances by impedance spectroscopy the entire system, i.e. the membrane, the electrolyte, and the electrodes are treated as a "black box". An alternating sinusoidal voltage of a given frequency and amplitude is applied to the system. The resulting current is measured, and then the phase shift compared to the input signal is determined. The procedure is repeated at different frequencies. An experimental set-up using the black box approach for determining the electrical resistance of ion-exchange membranes is illustrated in Figure 3.12.

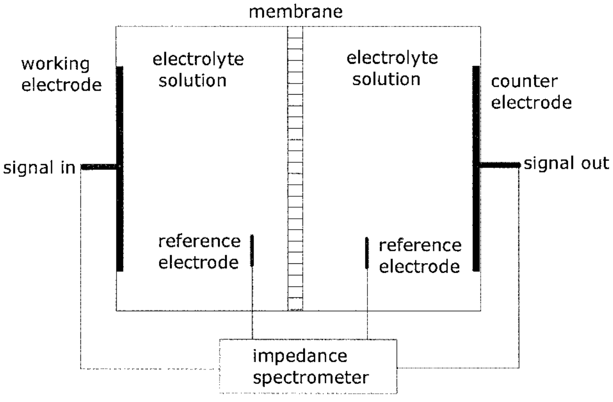


Fig. 3.12 Experimental setup using the "black box" approach for measuring the impedance of a system composed of a membrane, an electrolyte, and electrodes.

The figure indicates the signal input through the working electrodes and the output via the counter electrodes. In certain cases it is advisable to use reference electrodes to exclude electrode reactions in the "black box" measurement system.

The impedance is defined in analogy to Ohm's law to:

$$Z_{(\omega)} = \frac{U_{(\omega)}}{I_{(\omega)}} \tag{3.6}$$

with:

$$U_{(\omega)} = U_o \cos \omega t = U_o\, e^{i\omega t} \tag{3.7}$$

and

$$I_{(\omega)} = I_o \sin \omega t + \varphi = I_o\, e^{i(\omega t + \varphi)} \tag{3.8}$$

Here Z is the impedance, U is the voltage and ω is the circular velocity which is also referred to as circular frequency of the alternating current, t is the time, φ is the phase shift between voltage and current, and the subscript o refers to the amplitude of voltage and current, and (ω) refers to a certain circular velocity. The circular velocity ω is a function of the frequency ν, and is given by:

$$\omega = 2\,\pi\nu \tag{3.9}$$

Furthermore is:

$$Z_{total} = Z_1 + Z_2 + \ldots.. Z_n \tag{3.10}$$

for impedances in series,

and

$$\frac{1}{Z_{total}} = \frac{1}{Z_1} + \frac{1}{Z_2} + \ldots\ldots \frac{1}{Z_n} \tag{3.11}$$

for impedances in parallel.

The impedance is given by the relation between the voltage and current:

$$Z_{(\omega)} = \frac{U_{(\omega)}}{I_{(\omega)}} = Z\, e^{-i\varphi} = Z\, \cos\varphi - i\, Z\, \sin\varphi \tag{3.12}$$

Equation 3.12 indicates that the impedance is composed of two parts, i.e. the real part given by Z cos φ and the imaginary part given by iZ sin φ.

The impedance related to an electric resistance and to a capacitance are different. For an electric resistance the imaginary part of the impedance is zero since the current and voltage are in phase and the real part is frequency independent.

$$Z = \frac{U_o}{I_o} = R \tag{3.13}$$

For a capacitance the impedance is given by:

$$Z = \frac{1}{i\,\omega\, C} \tag{3.14}$$

A capacitor is characterized by the phase shift between current and voltage with a phase angle of $\pi/2$. Thus the impedance of a capacitance is frequency dependent and imaginary.

To obtain information about the dynamic behavior of a system two different graphic illustrations are used. In one graph the two different parts of the impedance, i.e. the real and the imaginary part are shown as a function of the frequency. This graph is referred to as the complex plain plot, or the Argand-diagram. In the second graph, the so-called Bode-diagram, the impedance and the phase angle are shown as a function of the frequency.

A typical complex plain plot obtained for a system containing resistances and capacitance in series and in parallel are shown in Figures 3.13 a) and b).

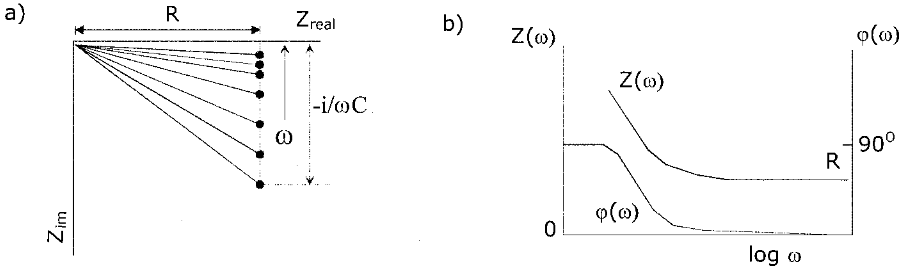


Fig. 3.13 Results of the impedance measurements of a system with resistance and capacitance in series shown schematically a) in a complex plain plot and b) in the Bode diagram.

The total impedance for a resistance and a capacitance in series is:

$$Z_{(\omega)} = R + \frac{1}{i\,\omega\,C} \tag{3.15}$$

According to Equation 3.15 and the graphs a) and b) in Figure 3.13 the imaginary part will disappear at very high frequencies if resistance and capacitance are in series and the impedance is identical to the ohmic resistance. At very low frequencies the impedance of the capacitance increases with decreasing frequency and becomes infinitely high in direct current.

For resistance and capacitance in parallel the total impedance is given by:

$$Z_{(\omega)} = \frac{R}{1+\omega^2 R^2 C^2} - i\frac{\omega\,R^2 C}{1+\omega^2 R^2 C^2} \tag{3.16}$$

The results are shown in Figure 3.14 a) and b).

According to Equation 3.13 and the graphs in Figure 3.14 a) and b) the imaginary part of the impedance disappears at very low and very high frequencies. At very low frequency all current is passing through the resistance and the impedance is identical to the electric resistance. At very high frequencies both the imaginary and the real part of the impedance approach zero. With increasing frequency the phase shift between current and voltage is increasing and with the phase shift the imaginary part of the impedance is increasing and reaches a maximum at a frequency of $\omega=1/RC$. A further increase in frequency will increase the phase shift but will decrease the imaginary part of the impedance. This is indicated by the semi-circular curve in the diagram of Figure 3.14 a).

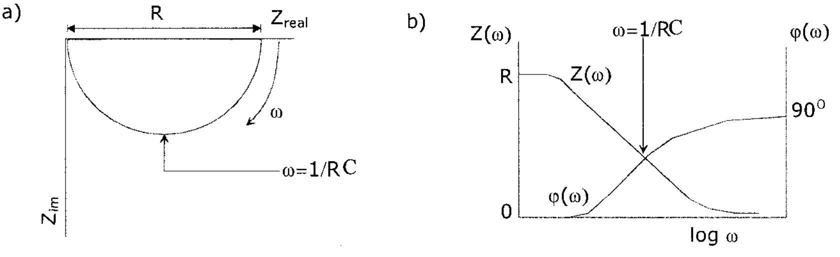


Fig. 3.14 Results of the impedance measurements of a system with resistance and capacitance in parallel shown schematically a) in the complex plain plot and b) in the Bode diagram.

In a system composed of an ion-exchange membrane, an electrolyte, and two electrodes there may be both resistances and capacitances in series and in parallel and the impedance can be rather complex and it is not always easy to determine the membrane resistance from the obtained diagram, and mathematical models may be used to obtain reliable data for the membrane resistance.

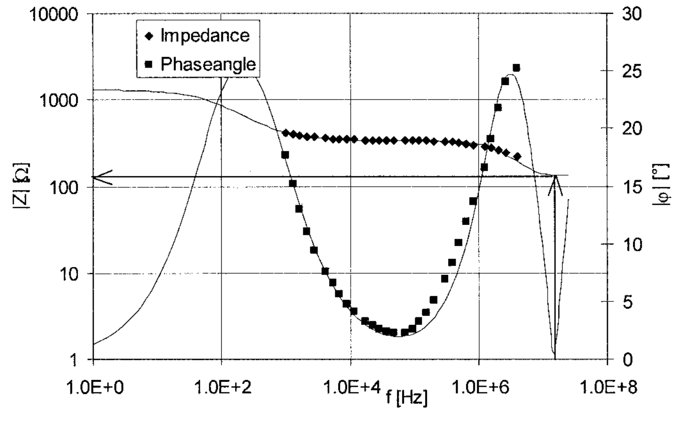


Fig. 3.15 Bode diagram of an impedance spectrum determined in a 0.5 mol/L sodium acetate solution with a CM-1 cation-exchange membrane manufactured by Tokuyama Soda.

Figure 3.15 shows the Bode plot of an impedance spectrum determined in a 0.5 mol/L sodium acetate solution with a CM-1 cation-exchange membrane manufactured by Tokuyama Soda. At a frequency of 815 kHz the phase angel approaches zero and the resistance is 118 Ω.

The practical determination of the impedance spectra can be carried out in the test cell shown in Figure 3.16 following the same procedure as in measurements with alternating current described earlier.

Generally, the measurements are carried out with and without a membrane in the test cell. The membrane resistance is calculated from the difference of the impedance determined with and without the membrane. Often, the specific resistance of the membrane is of the same order as that of the electrolyte solution. Therefore, the difference in the resistance of the cell with and without membrane is small compared to the overall resistance. Thus, for the relatively thin membrane the resistance must be determined from a small difference between two large numbers. This effects the accuracy of the calculated membrane resistance. To obtain more reliable data a stack of membranes is placed in the cell and the resistance of a single membrane is determined by dividing the resistance of the membrane stack by the number of membranes. This method results in more reliable data for membranes with smooth surfaces. It is not suited for membranes with very rough surfaces such as membranes reinforced by a screen. To avoid the problems related to determining the membrane resistance as a small difference between to large numbers from measurements in electrolyte solutions the test membrane is placed between two contact membranes and the working electrodes which also serve as reference electrodes placed directly on the surface of the membrane assembly as in Figure 3.16. The figure shows the cross-section of a test cell. The contact membranes should be homogeneous and unsupported and should have a relatively soft surface to provide good contact between the electrodes and the test membrane. The test membrane and the two contact membranes must have the same electrical charges and must be equilibrated in the test solution. The impedance measurement is carried out with the test membrane and without the test membrane and the resistance of the test membrane is obtained as the difference of the resistance measurements.

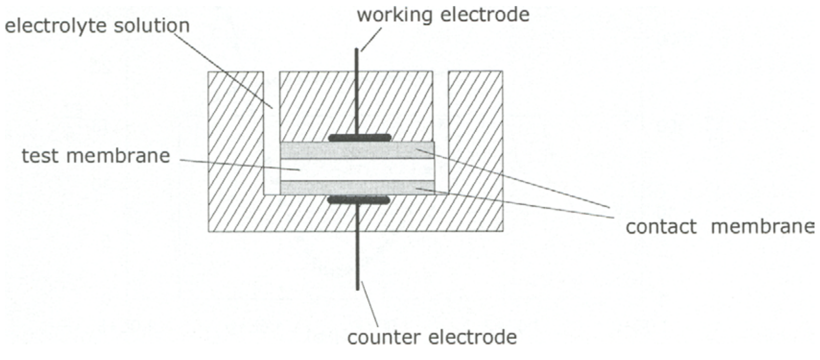


Fig. 3.16 Schematic drawing of the test cell cross-section used for the impedance measurements.

The determination of the membrane resistance by impedance measurements is a rather reliable and fast method which is especially suited for routine testing of homogeneous membranes having a smooth surface. In contrast to direct current measurements boundary layer effects caused by differences in the transport rate of ions in the membrane and in the solution at the membrane surface are excluded and thus do not effect the measurement. However, the membrane resistances determined with impedance measurements are generally significantly lower for heterogeneous and reinforced membranes than those measured in tests with direct current for reasons that have been explained earlier. As data base for the design of electrodialysis stacks the resistances determined in direct current measurements are better suited than those determined by impedance measurements.

3.3.3 Permselectivity of Ion-Exchange Membranes

The permselectivity of a membrane is determined by the ratio of the flux of specific components to the total mass flux through the membrane under a given driving force. In ion-exchange membranes the permselectivity is generally related to the transport of electric charges by the counterions to the total electrical current through the membrane. However, the transport rate of different components of the same charge in ion-exchange membranes can also be quite different because of kinetic parameters such as the size of the components and the structure of the membrane. The permselectivity of an ion-exchange membrane, i.e. its charge selectivity is determined by the concentrations of counter- and coions in the membrane, which again depends mainly on the ion-exchange capacity of the membrane and the ion concentration in the outside solutions because of the Donnan exclusion as discussed earlier. The permselectivity can be calculated from the transport or transference number of the counter- and coions in the membrane and the outside solutions.

The permselectivity of a membrane is given by Equation 2.174 to:

$$\Psi^{m} = \frac{T_{cou}^{m} - T_{cou}}{T_{co}} \tag{3.17}$$

The transport numbers are defined by Equation 2.102 to:

$$T_i = \frac{z_i\, J_i}{\sum\limits_i z_i\, J_i} \tag{3.18}$$

Here Ψ is the permselectivity, T is the transport number, z is the valence, and J is the flux; the subscript i refers to cation or anion, the subscripts cou and co refer to counter- and coions and the superscript m refers to ion-exchange membrane. In a cation-exchange membrane the cation is the counterion and the anion the coion while in an anion-exchange membrane the anion is the counterion and the cation the coion.

An ideal permselective cation-exchange membrane, for instance, would be permeable for positively charged cations (counterions) only. The permselectivity of a membrane approaches zero when the transport numbers of the ions within the membrane are identical to those in the electrolytic solution.

To determine the transport number of ions in the membrane and the membrane permselectivity, respectively, two methods can be applied. The first method is based on a measurement of the increase in concentration of certain ions in the concentrate and the decrease in the diluate solution during electrodialysis of a test solution and by measuring the amount of current passing through the unit. From the current utilization the permselectivity of the membrane and the transport number of the counterion can be calculated. With this "dynamic" measurement water transport due to electroosmosis and osmosis is taken into account and the "true" membrane permselectivity is obtained. The dynamic method, however, is rather time consuming and effected by concentration polarization at the membrane surfaces facing the diluate and concentrate solutions.

A faster "static" method for the determination of membrane permselectivities, which is not effected by boundary layer transport phenomena, is based on the measurement of the potential gradient across a membrane which separates two electrolyte solutions of different concentrations. The static method, however, does not take the water transport through the membrane into account and is referred to as "apparent" permselectivity.

The potential between two electrolyte solutions of different concentrations, i.e. the membrane potential has been discussed earlier and it is illustrated in Figure 2.18 and consists of the two Donnan potentials between the membrane and the adjacent solutions and the diffusion potential across the membrane.

$$\varphi_m = \varphi_{dif} + \varphi^1_{Don} - \varphi^2_{Don} \tag{3.19}$$

Here φ is the potential, the subscripts m, dif, and Don refer to membrane, diffusion, and Donnan potential, and the superscripts 1 and 2 refer to the different solutions.

The diffusion potential is caused by the transport of co-ions, i.e. salt diffusion through the membrane. It is the result of the different permeability of the cation and anion in an ion-exchange membrane. For a completely permselective membrane the salt diffusion and thus, the diffusion potential, is zero. The membrane potential is then given by the difference in the two Donnan potentials. For a not strictly permselective membrane the diffusion potential must be added to the Donnan potential difference to determine the membrane potential. For a single, monovalent salt such as KCl as an electrolyte the membrane potential between two solutions of the same electrolyte but different concentration can be derived from the general flux equation described earlier with the boundary conditions of $\Delta P = 0$ and $I = 0$. By introducing several approximations, such as negligible osmotic flow between the two solutions, constant ion mobility, and small concentration gradients across the membrane phase etc., the potential difference between solutions can be expressed by:

$$\varphi_m = \left(T^m_{cou} - T^m_{co}\right)\frac{RT}{F}\ln\frac{a^1_s}{a^2_s} = \left(2T^m_{cou} - 1\right)\frac{RT}{F}\ln\frac{a^1_s}{a^2_s} \tag{3.20}$$

For a strictly permselective membrane the transport number of the counter-ion is 1, i.e. there is no salt diffusion through the membrane, and the membrane potential is given by:

$$\varphi_{m,sp} = \frac{RT}{F}\ln\frac{a^1_s}{a^2_s} \tag{3.21}$$

Here are φ_m and $\varphi_{m,sp}$ the membrane potentials of a real and a strictly permselective ion-exchange membrane, T^m_{cou} and T^m_{co} are the transport numbers of the counter- and coions in the membrane, a_s is the activity of the salt solution, R is the gas constant, T is the temperature, F is the Faraday constant and the superscripts 1 and 2 refer to the two solutions separated by the membrane.

The counterion transport number in a not strictly permselective membrane is obtained as follows:

$$\frac{\varphi_m}{\varphi_{m,sp}} = 2T^m_{cou} - 1 \tag{3.22}$$

and

$$T^m_{cou} = \frac{\dfrac{\varphi_m}{\varphi_{m,sp}} + 1}{2} \tag{3.23}$$

Introducing Equation 3.23 into Equation 3.17 and rearranging gives the permselectivity of a cation-exchange membrane as a function of the membrane potential:

$$\Psi^m = \frac{\dfrac{\varphi_m}{\varphi_{m,sp}} + 1 - 2T_{cou}}{2T_{co}} \tag{3.24}$$

Here Ψ^m is the apparent permselectivity of an ion-exchange membrane.

For a salt such as KCl the transport numbers of cation and anion in the solution are nearly identical, i.e. $T_{cou} \cong T_{co} \cong 0.5$ and the permselectivity can be expressed to a first approximation by:

$$\Psi^{cm} \cong \frac{\varphi_{m,real}}{\varphi_{m,sp}} \tag{3.25}$$

The membrane potential is measured with reference electrodes in a test cell consisting of two chambers separated by a membrane as illustrated in Figure 3.17.

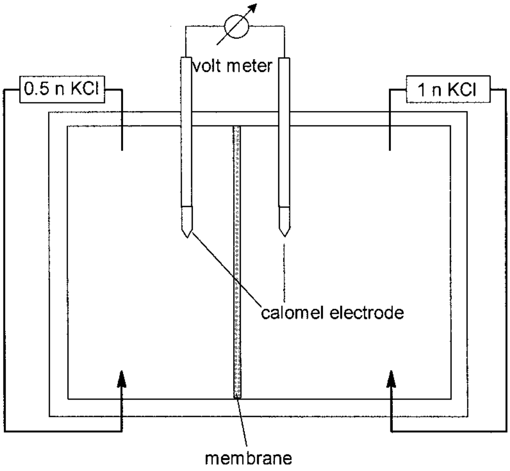


Fig.3.17 Schematic drawing illustrating the test cell for determining the membrane potential.

Both chambers are filled with the same electrolyte solution, e.g. KCl but with different concentrations, i.e. 0.5 and 1 mol L^{-1}. To avoid a concentration change due to diffusion the two solutions are well mixed. Then the membrane potential is measured and divided by the potential of a strictly permselective membrane at 25°C which is calculated by Equation 3.21 for the above given electrolyte concentration to:

$$\varphi_{m,sp} = \frac{RT}{F}\ln\frac{a_i^1}{a_i^2} = \frac{RT}{F}\ln\frac{C_i^1}{C_i^2}\frac{\gamma_i^1}{\gamma_i^2} = 0.02569\ln\frac{1}{0.5}\frac{0.6}{0.65} = 0.0158\,[\text{Volt}] \qquad (3.26)$$

Here γ_i^1 and γ_i^2 are the activity coefficients of KCl in the two solutions separated by the membrane which are obtained from the literature. The permselectivity of a membrane is according to Equation 3.25:

$$\Psi^m \cong \frac{\varphi_{m,real}}{0.0158} \qquad (3.27)$$

This is the apparent permselectivity of a membrane which is always larger than the real permselectivity since it does not take into account the water transport due to osmosis and electroosmosis. However, the difference between the apparent and real permselectivity is generally very small. As an advantage, the determination of the potential between two solutions of different concentrations is not effected by concentration polarization at the membrane surface. For characterizing membrane samples in manufacturing processes the static method is generally applied.

3.3.4 Membrane Permeation Selectivity for Different Counter-Ions

The permeation of counter- and co-ions in ion-exchange membranes is generally quite different and the counter-ion permselectivity is close to 1. It is determined mainly by the Donnan exclusion of the co-ions. However, certain ion-exchange membranes also show a permeation selectivity for different counter-ions. This selectivity is determined mainly by the mobility of the different ions in the membrane, i.e. by the ion size and the structure of the membrane. The permeation selectivity of different counterions is determined by measuring the fluxes of counterions in a mixture of electrolytes having different counterions but identical coions with reversible electrodes, or in a conventional electrodialysis test. The permeation selectivity of a membrane for different counter-ions is given by the ratio of their fluxes through the membrane which is identical to the ratio of their transport numbers in the membrane.

3.3.5 Diffusion Coefficients of Electrolytes in Ion-Exchange Membranes

When ion-exchange membranes are used in electrodialysis or diffusion dialysis one side of the membrane is in contact with a concentrated solution and the other side with a diluted solution. In practical applications often large concentration gradients across the membrane are obtained which results in a diffusion of low molecular weight charged and non-charged components through the membrane. The diffusion of charged components effects the current efficiency and leads eventually to a contamination of the product or to a loss of valuable components when certain biological materials are treated. The determination of the diffusion coefficients can be carried out by standard procedures such as the time-lag method [J. Crank et al., 1968]. In the time-lag experiment the membrane separates two solutions. One solution contains the test component in a certain concentration while the other solution and the membrane are free of this component. Then the flux through the membrane is measured as a function of time. In a first stage of the measurement, the so-called transition state, the flux is increasing exponentially with time. After a certain time the flux increase with time becomes linear and the system has reached a steady state. At steady state the mass flux is given by:

$$M_t = \frac{DC_o}{l}\left(t - \frac{l^2}{6D}\right) \tag{3.28}$$

Here is M_t the steady state mass flux of the test component through the membrane, C_o is its original concentration in the feed solution, l is the thickness of the membrane, and D is the diffusion coefficient of the test component in the membrane.

If the linear part of the plot of $\frac{M_t}{lC_o}$ versus time is extrapolated to the time axis of the diagram as shown schematically in Figure 3.18 the resulting intercept L is referred to as time-lag L which is given by:

$$L = \frac{l^2}{6D} \tag{3.29}$$

For a given membrane thickness l the diffusion coefficient can be determined from Equation 3.29:

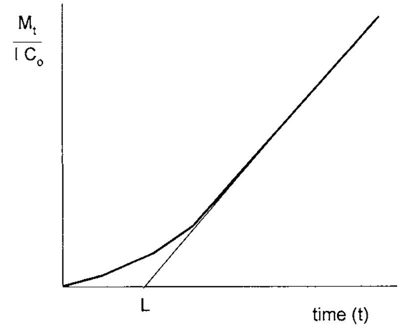


Fig. 3.18 Schematic drawing illustrating the determination of diffusion coefficients by the time-lag method.

The time-lag method is very convenient for the determination of diffusion coefficients. However, the results can be obscured by osmotic water transfer due to large concentration gradients across the membrane. To eliminate such effects radioactive tracer techniques may be used.

3.3.6 Water Transport in Ion-Exchange Membranes

The water transport through ion-exchange membranes is caused by osmosis and by electroosmosis. The osmotic water transport is the result of concentration differences between the two solutions separated by the membrane. Electroosmosis refers to the water transported in the hydration shell of the ions migrating through the membrane due to an electrical potential gradient. The osmotic water transport is measured using a two compartment cell containing pure water in one compartment separated from the second compartment containing a concentrated solution. The volume change in the compartments is determined as a function of time in two horizontal capillaries connected with the compartments as indicated in the schematic drawing of Figures 3.19 and 3.20 which illustrate the experimental set-up to determine the water transport in osmosis and electroosmosis.

In osmotic water transport measurements one cell is filled with water and the other with a salt solution. The water flux from the cell filled with water into that filled with the solution is measured in the horizontally arranged capillaries as indicated in Figure 3.19. Since the osmotic pressure is a linear function of the concentration of a solution the osmotic water transport increases linearly with the salt concentration.

The electroosmotic water transport is expressed by a transport number in analogy to the transport number of ions and is given by:

$$T_w^m = \frac{F\,J_w}{i} \tag{3.30}$$

Here is T_w^m the transport number of water through a membrane, F is the Faraday constant, i is the current density, and J_w is the water flux expressed in moles per unit area and time.

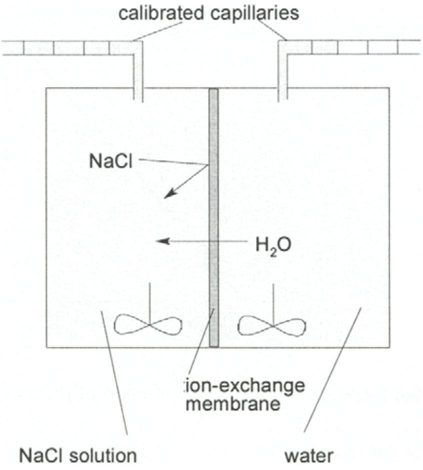


Fig. 3.19 Schematic drawing illustrating the test cell for determining the osmotic water flux through an ion-exchange membrane.

In the electroosmotic water transport measurement a direct current is applied using reversible electrodes, i.e. Ag/AgCl-electrodes. Both compartments of the test cell are filled with a test solution of identical concentrations. The electroosmotic water transport of a cation-exchange membrane is a function of the migration of the cation and is determined by water connected to the ion in its hydration shell. The electroosmotic water transport through a cation-exchange membrane due to the migration of a Na^+-ion can be determined by measuring the volume change in the two compartments of a test cell filled with a NaCl-solution as indicated schematically in Figure 3.20.

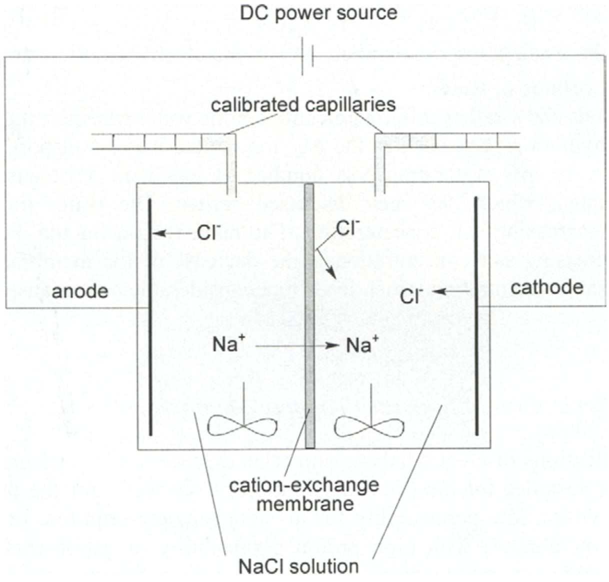


Fig. 3.20 Schematic drawing illustrating the test cell to determine the electroosmotic water transport.

In the test it is assumed that the membrane is strictly semipermeable, i.e. it is only permeable for Na^+-ions. However, the volume in the two compartments of the cell is not only the result of the water transport. The volumes of the cells are also changed by the electrode reactions. At the anode Cl^--ions disappear and at the cathode Cl^- -ions are generated according to the following reaction scheme:

$$\text{anode: } Ag + Cl^- \rightarrow AgCl + e$$

and

$$\text{cathode: } AgCl + e \rightarrow Ag + Cl^-.$$

The electroosmotic water transport is calculated from the volume change in the two compartments:

$$\Delta V_F = \Delta V_{tot} + \overline{V}_{AgCl} - \overline{V}_{Ag} - \overline{V}_{Cl^-} = T^m_{Na^+} n_w^{Na^+} + \overline{V}_{Na^+} \tag{3.31}$$

Here ΔV_{tot} and ΔV_F are the total volume change and the volume change due to electroosmosis in the cell when electrical charges of 1 Faraday are transported, $\overline{V}$ is the partial molar volume of AgCl and Ag, and T_{Na}^m is the transport number of Na^+-ions in the membrane, and $n_w^{Na^+}$ is number of water molecules carried by on Na^+-ion.

The electroosmotic water flux is:

$$\Delta V_F = T_w^m \overline{V}_w \tag{3.32}$$

Here is T_W^m the water transport number, ΔV_F is the electroosmotic water flux, and $\overline{V}_w$ is the partial molar volume of water.

Different cations show rather different electroosmotic water transport numbers. Ions with a relatively large hydration shell such as the Na^+-ion have a water transport number of 6 to 8. Protons have a very low water transport number of less than 3 because of the different transport mechanism which has been discussed earlier. The water transport number is decreasing with increasing salt concentration. The main reason for the decreasing transport number with increasing salt concentration is the decrease of the membrane permselectivity with increasing salt concentration which leads to a considerable coiontransport in the opposite direction.

3.3.7 Characterization of Special Property Membranes

In many applications of electrodialysis and related processes special property membranes are required. For instance for the pre-concentration of sea water for the production of table salt membranes with a low permeability for divalent ions are required. In diffusion dialysis anion-exchange membranes with high proton permeability or cation-exchange membranes with high hydroxide ion permeability are needed, and in bipolar membrane applications generally acid and base blocking mono-polar membranes as well as efficient bipolar membranes with a low electric resistance and good water dissociation capability are needed [G. Pourcelly et al., 1993, 1994]. Most mono-polar membranes can be characterized by applying the procedures described earlier. In addition to the electrical resistance and the permselectivity the water dissociation capability is for bipolar membranes of prime importance. Therefore, membranes are generally characterized by a so-called current versus voltage plot. Determination of the current through a bipolar membrane as a function of the applied voltage provides information about the water dissociation, the electrical resistance, and the salt leakage of the membrane. A typical current versus voltage curve of a commercial bipolar membrane is shown in Figure 3.21 a) and b) [J.J. Krol et al., 1998].

The Figure 3.21 a) shows the current density as a function of the voltage applied across the commercial bipolar membrane in a 1mol L^{-1} Na_2SO_4 solution. At low voltage between 0 and 0.1 V the current increases linearly with the applied voltage to about 1 to 2 mA cm^{-2}. A further increase of the voltage across the membrane does not lead to a significant current increase until a voltage drop of 0.6 to 0.8 Volt is reached. Then the current increases sharply to about 200 to 400 mA cm^{-2} with increasing applied voltage until a voltage of ca. 1 V is reached. A further increase in voltage does not increase the current significantly and generally leads to a destruction of the membrane.

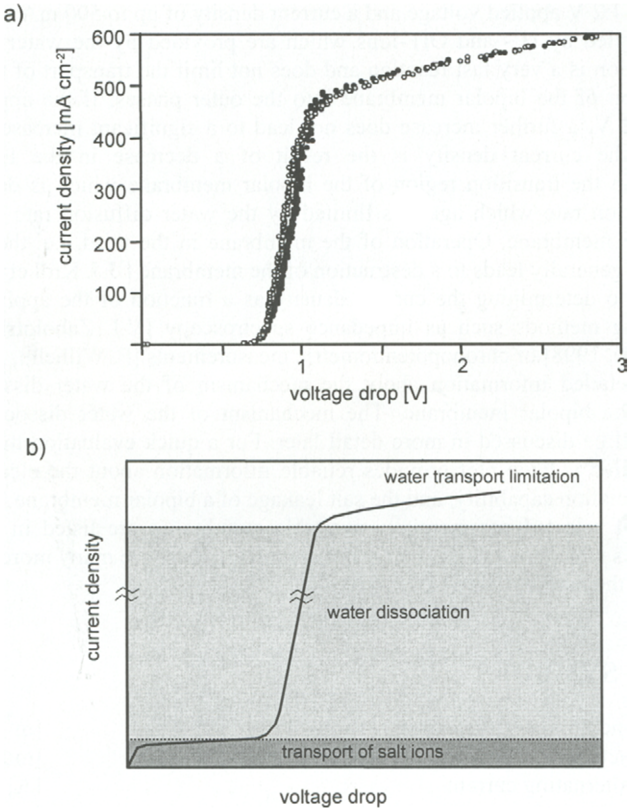


Fig. 3.21 Current density versus applied voltage curve a) measured with a commercial bipolar membrane in a 1 mol L^{-1} Na_2SO_4 solution and b) schematic drawing indicating 3 distinct areas where the current is determined by the salt transport, the water dissociation, and by the water diffusion into the reaction zone of the membrane.

As illustrated in the schematic drawing of Figure 3.21 b) three distinct areas in the current versus voltage curve can be identified. The first area is characterized by a linear increase in current with the applied voltage until a limiting value of ca. 1 mA cm^{-2} is reached at ca 0.1 V. A further increase in the applied voltage does not lead to an increase in the current. The current in this region is the result of salt transport from the transition region of the bipolar membrane into the outside solutions due to the driving force of the applied potential. Up to an applied voltage of ca. 0.1 V this transport is compensated by salt diffusion from the outside solutions into the bipolar membrane due to a concentration gradient. The salt transport out of the membrane can not exceed the diffusive salt transport into the membrane independent of the applied voltage. Thus, a steady state is reached and the current is limited by the salt diffusion into the membrane until the voltage drop across the membrane reaches 0.6 to 0.8 V. The drastic current increases when the applied voltage is increased further, is the result of the transport of H^+- and OH^--ions that are produced within the bipolar membrane. In the region between 0.5 to 1.2 V applied voltage and a current density of up to 500 mA cm^{-2} the current is exclusively carried by H^+- and OH^--ions which are provided by the water dissociated. The water dissociation is a very fast reaction and does not limit the transport of the ions from the transition region of the bipolar membrane into the outer phases. If the applied voltage has reached ca. 1.2 V, a further increase does not lead to a significant increase in current. This limitation of the current density is the result of a decrease in the H^+- and OH^--ion concentration in the transition region of the bipolar membrane which is determined by the water dissociation rate which again is limited by the water diffusion rate from the outside phases into the membrane. Operation of the membrane in the third, i.e. the water diffusion limited region, generally leads to a destruction of the membrane [J.J. Krol et al., 1998].

In addition to determining the current density as a function of the applied voltage more complex testing methods such as impedance spectroscopy [V.I. Zabolotsky et al., 1978], [H. Holdik et al., 1998] or chronopotentiometric measurements [F. Wilhelm, 2001] are used to obtain more detailed information about the mechanism of the water dissociation and the resistance of the bipolar membrane. The mechanism of the water dissociation in bipolar membranes will be discussed in more detail later. For a quick evaluation the current density versus the applied voltage plot provides reliable information about the electrical resistance, the water dissociation capability, and the salt leakage of a bipolar membrane.

Properties of selected commercially available membranes are listed in the Table.of the Appendix I This table, however, is by far not complete. There are many more special property membranes on the market today.

4 LIST OF SYMBOLS

A_m	membrane surface area	[m^{2}]
a	activity	[mol m^{-3}]
AC	alternating current	[A]
C	concentration	[mol m^{-3}]
D	diffusion coefficient	[m^{2} s^{-1}]
DC	direct current	[A]
d	distance	[m]
d_m	membrane thickness	[m]
i	current density	[A m^{-2}]
J	flux	[mol m^{-2} s^{-1}]
L	time lag	[s]
l	distance	[m]
M_t	steady state mass flux	[mol m^{-2} s^{-1}]
N	number of moles	[mol]
R	resistance	[Ω]
R	gas constant	[J mol^{-1} ^{o}K]
T	temperature	[^{o}K]
T	transport number	[-]
t	time	[s]
V	volume	[m^{3}]
$\overline{V}$	partial molar volume	[m^{3} mol^{-1}]
U	voltage drop	[V]

r	area resistance	[Ω cm^2]
W	weight	[kg]
z	valence	[eq mol^{-1}]
Z	impedance	[Ω]

Greek letters

ρ	specific resistance	[Ω m]
Ψ	permselectivity	[-]
ω	circular velocity	[s^{-1}]
ν	frequency	[s^{-1}]
φ	phase shift angle	[degree]

subscripts

i	refers to component
cou	counter-ion
co	coion
m	membrane
s	solution

LITERATURE

Asahi Chemical 1990. Product Bulletin, Tokyo, Japan.

Asahi Glass 1990. Product Bulletin, Tokyo, Japan.

Bauer, B., 1993. Bipolar membrane and process of its preparation, European Patent 056851

Bauer, B., Effenberger, F., Strathmann, H.. 1990. Anion-exchange membranes with improved alkaline stability, Desalination, 79:125-144.

Bauer, B., Gerner, F.-J., Strathmann, H., 1988. Development of bipolar membranes, Desalination 68: 279-292.

Bergsma, F., Kruissink, CH.A., 1961. Ion-exchange membranes, Fortschr. Hochpolym.-Forsch., 21: 307-362.

Caplan, S.R., Sollner, K., 1974. Influence of the characteristics of the activating polyelectrolyte in the preparation and on the properties of interpolymer ion-exchange membranes: rational principles of membrane preparation and their experimental test, J. Colloid Interface Sci., 40: 46-66.

Chlanda, F.P., Lee,L.T.C., Liu, K.J., 1976. Bipolar membranes and method of making the same, U.S. Patent 4,116,889.

Connolly, D.J., Gresham, W.F., 1966. Fluorocarbon vinylether polymers, U.S. Patent 3,282,875.

Coulter, M.V., 1980. Modern chlor-alkali technology, Ellis Horwood Ltd., Chichester, U.K.

Crank, J., Park, G.S., 1968. Diffusion in polymers, Academic Press, London.

Cui, W., Kerres, J. Eigenberger, G., 1998. Development and characterization of ion-exchange polymer blend membranes, Separation & Purification Technology, 14: 145-154.

Davis, T.A., Genders, J.D., Pletcher, D.,1997. Ion permeable membranes, Alresford Press Ltd. Alresford, Hants, England.

De Korocy, F., Zeigerson, E., 1967 Investigation by electron microscopy and x-ray diffraction of the microstructure of permselective membranes made of polyethylene, J. Appl. Polymer Sci., 11: 909-919.

Dohno, R., Azumi, T., Takashima, 1975. Permeability of monocarboxylate ions across an anion-exchange membrane, Desalination, 16: 55-64.

Dotson, R.L., Woodard, K.E., 1982. Electrosynthesis with perfluorinated ionomer membranes in chlor-alkali cells, in: Perfluorinated ionomer membranes, edts.: Eisenberg, A., Yeager, H.L.. ASC-Symposium Series 180, American Chemical Society, Washington DC.

DuPont, 1988. Product Bulletin.

Eisenberg, A., Yeager, H.L., 1982. Perfluorinated ionomer membranes, in: Perfluorinated ionomer membranes, edts.: Eisenberg, A., Yeager, H.L., ASC-Symposium Series 180, American Chemical Society, Washington DC.

Escoubes, M., Pineri, M., 1982. Thermodynamic studies of the water-perfluorosulfonated polymer interactions, in: Perfluorinated ionomer membranes, edts.: Eisenberg, A., Yeager, H.L.. ASC-Symposium Series 180, American Chemical Society, Washington DC.

Falk, M., 1982. Infrared spectra of perfluorosulfonated polymer and of water in perfluorosulfonated polymer, in: Perfluorinated ionomer membranes, edts.: Eisenberg, A., Yeager, H.L.. ASC-Symposium Series 180, American Chemical Society, Washington DC.

Flett, D.S., 1983. Ion-exchange membranes, E. Horwood Ltd., Chichester, U.K.

Grot, W.G., 1973. Laminates of support material and fluorinated polymer containing pendant side chains containing sulfonyl groups, U.S. Patent 3, 770,567.

Grot, W.G., 1974. Films of fluorinated polymer containing sulfonyl groups with one surface in the sulfonamide or sulfonamide salt form and a process for preparing such, U.S .Patent, 3, 784, 399.

Grot, W.G., 1975. Perfluorinated cation exchange polymers, Chem.-Ing.-Tech., 47: 617.

Gudernatsch, W., Krumbholz, CH., Strathmann, H., 1990. Development of an anion-exchange membrane with increased permeability for organic acids of high molecular weight. Desalination 79: 249-260.

Haagen, K., Helfferich, F., 1959. Ionenaustauscher Membranen, German Patent 971729.

Hanada, F., Hiraya, K., Ohmura, N., Tanaka, S., 1991. Bipolar membrane and methode for its production, European Patent, 0459820.

Hanada, F., Hiraya, K., Ohmura, N., Tanaka, S., 1993. Bipolar membrane and methode for its production, US Patent 5, 221, 455.

Helfferich, F., 1962. Ion-exchange, McGraw-Hill, London.

Hodgdon, R.B., 1992. Aliphatic anion-exchange membranes having improved resistance to fouling, US Patent 5,137,925.

Hodgdon, R.B., Alexander, S.S., 1989. Novel bipolar membranes and process of manufacture, US-Patent 4 851 100, Hodgdon, R.B., Witt, E., Alexander, S.S., 1973. Synthesis and transport properties of macrorecticular anion-exchange membranes for electrodialysis in the presence of surface water foulants, Desalination, 13: 105-127.

Holdik, H., Alcaraz, A., Ramirez, P., Mafe, S, 1998. Electric field enhanced water dissociation at bipolar membrane junction from impedance spectroscopy, J. Electroanal. Chem., 442: 13-18.

Hurwitz, H., El Moussaoui, R., 1998. Single film membrane, process for obtaining it and use therefore, US Patent, 5 840 192.

Ionics Inc., 1990. Product Bulletin CR, Watertown, MA 02172.

Ishibashi, N., Seiyama, T., Sakai, W., 1954. Electrochemical studies on ion-exchangers, preparation of a cation-exchange membrane and its properties, J. Electrochemical Soc. Japan, 22: 684-687.

Ishigaki, I., Kamiya, N., Sugo, T., Machi, S.,1978. Synthesis of an ion-exchange membrane by radiation-induced grafting of acrilyc acid onto poly(tetrafluorethylene), Polym. J., 10: 513-519.

Itoh, H., Yoshizumi, T., Saeki, M., 1986. Sieving effect in electrodialysis with an ion-exchange membrane, J. Membrane Sci., 27:155-163.

Juda, W., McRae, W.A., 1950. Coherent ion-exchange gels and membranes, J. Amer. Chem. Soc. 72: 1044.

Juda, W., McRae, W.A., 1953. U.S. Patent 2, 636, 851.

Kasper, A. A., 1955. Electrolytically conductive membranes, US Patent 2,702,272.

Kerres, J.A., 2000. Development of ionomer membranes for fuel cells, J. Membrane Sci., 185: 3–27.

Kerres, J.A., Ullrich, A., Hein, M., 2001. Preparation and characterization of novel basic polysulfone polymers, J. Polymer Sci., Part A, Polymer chemistry, 39: 2874-2888.

Kobuchi, Y., Matsunaga, Y., Noma, Y., 1987. Application of ion-exchange membranes to the recovery of acids by diffusion dialysis and electrodialysis, in: Synthetic polymer membranes, edts.: B. Sedlaceek, J. Kahovec, W. de Gruyter & Co. Berlin.

Komoroski, R.A., Mauritz, K.A., 1982. Perfluorosulfonated ionomer membranes, edts: Eisenberg, A., Yeager, H.L., ASC Symposium Series 180, American Chemical Society, Washington, D.C.

Korngold, E., 1984. Electrodialysis: Membranes and mass transport, in: Synthetic membrane processes, edt.: Belfort, G., pp. 192-219, Academic Press, New York.

Korngold, E., De Körösy, F., Rahav, R., Taboch, M.F., 1970. Fouling of anion selective membranes in electrodialysis, Desalination, 8: 195-220.

Krol, J.J., Jansink, J.M., Wessling, M., Strathmann, H., 1998. Behaviour of bipolar membranes at high current density: Water diffusion limitation, Separation & Purification Technology, 14: 41-52.

Kunin, R., 1958. Ion-exchange resins, Wiley-Interscience, New York.

Kusomoto, K., Sata, T., and Mizutani, Y., 1976. Modification of anion-exchange membranes with polystyrene sulfonic acid, Polym. J., 8:225-226.

Liu, K.J., Chlanda, F.P., Nagasubramanian, K.J., 1977. Use of bipolar membranes for generation of acid and base: an engineering and economic analysis, J. Membrane Sci., 2: 109-124.

Mani, K.N., 1991. Electrodialysis water-splitting technology, J. Membrane Sci., 58: 117-138.

Matsui, K.,Tobita, E., Sugimoto, K., Kondo, K., Seita, T., Akimoto, 1986. Novel anion-exchange membranes having fluorocarbon backbone: preparation and stability, J. Appl. Polym. Sci., 32: 4137-4143.

McRae, W.A., Alexander, S.S., 1960. Sulfonating reagent and its use in preparing cation-exchange membranes, U.S. Patent 2,962,454.

Meares, P., 1983. Trends in ion-exchange membrane science and technology, in: Ion-Exchange Membranes, edts.: Flett, D.S., E. Horwood Ltd., Chichester, UK.

Mihara, K., Misumi, T., Miyauchi, H., Ishida, Y., 1973. Anion-exchange membranes with excellent permselectivity between anions with the same charge, Japan Patent 48-34676.

Miyamoto, Y., 1991. Fabrication of charge-mosaic membranes and their performance, Maku, 16: 233-238.

Molau, G.E., 1981. Heterogeneous ion-exchange membranes, J. Membr. Sci., 8: 309-330.

Onoue, Y., Mizutani, Y., Yamane, R., Takasaki, Y., 1961. Selectivity of cation-exchange membrane, for NaCl-$CaCl_2$ system, J. Electrochem. Soc. Japan, 29: 187-191.

Onoue, Y., Sata, T., Nakahara, A., Itoh, J., 1980. Process for preparing fluorine-containing polymers having carboxyl groups, U.S. Patent 4,200,711.

Pourcelly, G., Tugas, I., Gavach, C., 1993. Electrotransport of HCl in anion exchange membranes for the recovery of acids, J. Membrane Sci., 85: 195-204.

Pourcelly, G., Tugas, I., Gavach, C., 1994. Electrotransport of sulphuric acid in special anion-exchange membranes for the recovery of acids, J. Membrane Sci., 97: 99-107.

Rapp, H.-J., 1995. Die Elektrolyse mit bipolaren Membranen, Theorie und Anwendung. Universität Stuttgart, FRG.

Sata, T., 1972. Monovalent cation permselective exchange membrane, Kolloid-Z. u. Z. Polymere, 250: 980-982.

Sata, T., 1986. Recent trends in ion-exchange research, Pure & Appl. Chemistry 58: 1613-1626.

Sata, T., Yamane, R., Mizutani, Y., 1979. Modification of properties of ion-exchange membranes, J. Polymer Sci. Polymer Chem., 17: 2071-2085.

Sata, T., Motani, K., Ohaski, Y., 1983. Perfluorinated exchange membrane "Neosepta-F" and its properties. In: Ion Exchange Membranes, edt. Flett, D.S., E. Horwood Ltd., Chichester, U.K.

Sata, T., Ogura, S., Kishimoto, F., 1993. Properties of composite membranes from ion-exchange membranes and conducting polymers, J. Membrane Sci., 84: 259-269.

Sata, T., Yamaguchi, T., Matsusaki, K., 1995. Effect of hydrophilicity of ion-exchange groups of anion-exchange membranes on permselectivity between anions, J. Phys. Chem., 99: 12875-12882.

Sata, T., Yamaguchi, T. Kawamura, K., Matsusaki, K., 1997. Transport numbers of various anions relative to chloride ions in modified anion-exchange membranes during electrodialysis, J. Chem. Soc. Faraday Trans. 93: 457-462.

Seko, M., Ogawa, S., Kimoto, K., 1988. Perfluorocarboxylic acid membrane and membrane chlor-alkali process developed by Asahi Chemical Industry. In: "Perfluorinated ionomer membranes", edts.: Eisenberg, A., Yeager, H.L.. ASC-Symposium Series 180, American Chemical Society, Washington, D.C.

Shel'deshov, N.V., Zabolotsky, V.I., Pis'menskaya, N.D. Gnusin, N.P., 1986. Catalysis of water dissociation by the phosphoric acid groups of an MB-3 bipolar membrane, Elektrokhimiya, 22: 791-795.

Simons, R. 1993. Preparation of a high performance bipolar membrane, J. Membrane Sci., 78: 13-23.

Simons, R., 1984. Electric field effects on proton transfer between ionizable groups and water in ion-exchange membranes, Electrochemica Acta, 29:151-158.

Simons, R., 1986. A novel method for preparing bipolar membranes, Electrochimica Acta, 31: 1175-1176.

Spiegler, K.S., 1958. Transport process in ionic membranes, Trans. Faraday Soc., 54: 1408-1428.

Spiegler, K.S., Laird, A.D.K., edts., 1980. Principles of desalination, 2nd edition, Academic Press, New York.

Strathmann, H., 1995. Electrodialysis and related processes, in: Membrane Separation Technology, edts.: Nobel, R.D., Stern, S.A. pp 213-281, Elsevier, Amsterdam.

Strathmann, H., Bauer, B., Rapp, H.J., 1993. Better bipolar membranes, CHEMTECH, June 1993: 17-24.

Suryanarayana, N.P., Krishnaswamy, 1963. Ion-exchange membranes based on rubber, J. Polym. Sci., Part B. 1: 491-495.

Gierke, T.D., Munn, G.E., Wilson, F.C., 1982. Morphology of perfluorosulfonated membrane products, in: Perfluorinated ionomer membranes, edts.: Eisenberg, A., Yeager, H.L.. ASC-Symposium Series 180, American Chemical Society, Washington DC.

Tokuyama Soda, 1987, 1988. Product Bulletin, Tokyo, Japan.

Tooper, E.B., Wirth, L.F., 1956. Ion-exchange resins, in: Ion-exchange technology, edts.: Nachod, F.C., Schubert, J., Academic Press, New York.

Wilhelm, F.W., 2000. Bipolar membrane preparation, in: Bipolar membrane technology, edt.: Kemperman, A.J.B., Twente University Press, Enschede, The Netherlands, ISBN 9036515203.

Wilhelm, F.W., 2001. Bipolar membrane electrodialysis, PhD.-thesis Twente University, Enschede, The Netherlands, ISBN 9036515270.

Yamane, R., Mizutani, Y., Motomura, H., Izuo, R., 1964. Preparation of SO42- nonpermeable anion-exchange membrane, J. Electrochem. Soc. Japan, 32: 277-288.

Yamane, R., Izuo, R., Mizutani, Y., 1965. Permeability of the amphoteric ion-exchange membranes, J. Electrochem. Soc. Japan, 33: 589-593.

Yeager, H.L., 1982. Cation-exchange selectivity of perflurosulfonate polymer, in: Perfluorinated ionomer membranes, edts.: Eisenberg, A., Yeager, H.L.. ASC-Symposium Series 180, American Chemical Society, Washington DC.

Yokoyama, Y., Tanioka, A., Miyasaka, K., 1989. Preparation of a single bipolar membrane by plasma-induced graft polymerization, J. Membrane Sci., 43: 165-175.

Zabolotsky, V.I., Nikonenko, V.V., 1993. Effect of structural membrane inhomogeniety on transport properties, J. Membrane Sci., 79: 181-198.

Zabolotsky, V.I., Shel'deshov, N.V., Gnusin, N.P., 1978. Impedance of MB-1 bipolar membranes, Elektrokhimiya, 15: 1488-1493.

Zschocke, P., Quellmalz, D., 1985. Novel ion-exchange membranes based on an aromatic polyethersulfone, J. Membrane Sci., 22: 325-332.