Recent developments on ion-exchange membranes and electro-membrane processes

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Abstract

Rapid growth of chemical and biotechnology in diversified areas fuels the demand for the need of reliable green technologies for the downstream processes, which include separation, purification and isolation of the molecules. Ion-exchange membrane technologies are non-hazardous in nature and being widely used not only for separation and purification but their application also extended towards energy conversion devices, storage batteries and sensors etc. Now there is a quite demand for the ion-exchange membrane with better selectivities, less electrical resistance, high chemical, mechanical and thermal stability as well as good durability. A lot of work has been done for the development of these types of ion-exchange membranes during the past twenty-five years. Herein we have reviewed the preparation of various types of ion-exchange membranes, their characterization and applications for different electro-membrane processes. Primary attention has been given to the chemical route used for the membrane preparation. Several general reactions used for the preparation of ion-exchange membranes were described. Methodologies used for the characterization of these membranes and their applications were also reviewed for the benefit of readers, so that they can get all information about the ion-exchange membranes at one platform.

Although there are large number of reports available regarding preparations and applications of ion-exchange membranes more emphasis were predicted for the usefulness of these membranes or processes for solving certain type of industrial or social problems. More efforts are needed to bring many products or processes to pilot scale and extent their applications.

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Keywords: Ion-exchange membranes; Charged membranes; Ionomers; Electro-membrane processes; Electrodialysis

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1. Introduction

Separation membranes have become essential parts of the human life because of their growing industrial applications in hi-tech areas such as biotechnology, nano-technology and membrane based energy devices in addition to different membrane based separation and purification processes. These processes are highly economically viable due to low energy requirements and facile scale-up of membrane modular design. Advances in membrane technology, especially in novel materials, can make this technology even more competitive with traditional, high-energy intensive, environmentally undesirable and costly processes. Various types of membranes have been developed for the use in reverse osmosis, nanofiltration, ultrafiltration, microfiltration, pervaporation, electrodialysis, solid polymer electrolyte, fuel cell applications, membrane based sensors, medical use such as artificial organs and controlled release, different ion-exchange membrane based electro-membrane processes [1]. Among these membranes, ion-exchange membranes are one of the most advanced separation membranes. The basic applications of the ion-exchange membrane process are based on the Donnan membrane equilibrium principle and have been paid attention to solve two important environmental problems, for the recovery and enrichment of valuable ions, and the removal of undesirable ions from waste water [2], especially to extract toxic metal ions from effluents [3]. Ion-exchange membranes discriminate cation and anions, thus they should have a high transport number for counter-ions. Such membranes have the potential applications as a new functional materials in separation of ionic materials, mostly used in the solutions containing multi components, such as electrodialytic concentration of seawater to produce sodium chloride, demineralization of saline water, desalination of cheese whey solutions, demineralization of sugarcane juice, etc. In some cases, because specific ions have been used industrially, monovalent ion permselective ion-exchange membranes [4–9], and proton permselective ion-exchange membranes are important [10,11]. Apart from these applications, several trials have been carried out, where ion-exchange membranes were used as sensors such as humidity sensor [12], carbon monoxide sensor [13], drug sensor [14], carriers for enzymes [15], solid polyelectrolytes [16], a carrier for functional materials [17], generation of photovoltage and photocurrent [18], which are new phenomena and might lead to new applications of the ion-exchange membranes.

For these wide applications, the most desired properties required for successful ion-exchange membranes are:

- High perm selectivity — an ion-exchange membrane should be highly permeable to counter-ion, but should be impermeable to co-ions.
- Low electrical resistance — an ion-exchange membranes should have low electrical resistance and thus there will be less potential drop during electro-membrane processes.
- Good mechanical 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 a pH-range from 0 to 14 and in the presence of oxidizing agents.
Properties of some commercially available membranes are listed in Table 1 [19–24]. This table, however, is far from being complete and subject to rapid change. Also there are many more special properties of these membranes listed in the table.

These parameters, determining the membrane properties often, have opposing effect. For example, a high degree of cross-linking improves the mechanical strength but increases the electrical resistance while more ionic charges in the membrane matrix lead to a low electrical resistance, but in general, cause a high degree of swelling combined with poor mechanical stability. Thus there is a compromise between these properties to develop good ion-exchange membranes. Herein, we are reviewing the different types of ion-exchange membranes, preparation procedure, characterizations and applications for diversified electro-membrane processes.

2. Preparation of ion-exchange membranes

Regarding chemical structure, ion-exchange membranes are very similar to the ion-exchange resins because both are bearing functional groups. The difference between membranes and resins arises largely from the mechanical requirement of the membrane process. Unfortunately, ion-exchange resins are mechanically weak, cation resins tend to be brittle, and anion resins soft. They are dimensionally unstable due to the variation in the amount of water imbibed into the gel under different circumstances. Changes in electrolyte concentration, and 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 that have been cut to fit an apparatus, they are not acceptable. Thus, it is generally not possible to use sheets of material that have 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 that gives the necessary strength and dimensional stability.

Most of the commercial ion-exchange membranes can be divided into two major categories, according to their structure and preparation procedure: homogeneous and heterogeneous. According to Molau [25], depending on the degree of heterogeneity of ion-exchange membranes can be divided into the following types: (a) homogeneous ion-exchange membranes, (b) interpolymer membranes, (c) micro-heterogeneous graft- and block-polymer membranes, (d) snake-in-the-cage ion-exchange membranes, (e) heterogeneous ion-exchange membranes [26].

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Structure properties</th>
<th>Ion-exchange capacity (meq/g)</th>
<th>Thickness (mm)</th>
<th>Water content (%)</th>
<th>Area resistance* (Ω cm²)</th>
<th>Permselectivity** (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tokuyama Soda Co. Ltd. Japan</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neosepta CMX Cation, PS/DVB</td>
<td>Homogeneous</td>
<td>1.5–1.8</td>
<td>0.14–0.20</td>
<td>25–30</td>
<td>1.8–3.8</td>
<td>97</td>
</tr>
<tr>
<td>Neosepta AMX Anion, PS/DVB</td>
<td>Homogeneous</td>
<td>1.4–1.7</td>
<td>0.12–0.18</td>
<td>25–30</td>
<td>2.0–3.5</td>
<td>95</td>
</tr>
<tr>
<td>Neosepta CMS Cation PS/DVB</td>
<td>Homogeneous</td>
<td>2.0</td>
<td>0.15</td>
<td>38</td>
<td>1.5–2.5</td>
<td></td>
</tr>
<tr>
<td>Neosepta ACM Anion PS/DVB</td>
<td>Homogeneous</td>
<td>1.5</td>
<td>0.12</td>
<td>15</td>
<td>4.0–5.0</td>
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<tr>
<td><strong>Asahi Glass Co. Ltd. Japan</strong></td>
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<tr>
<td>CMV Cation PS/DVB</td>
<td>Homogeneous</td>
<td>2.4</td>
<td>0.15</td>
<td>25</td>
<td>2.9</td>
<td>95</td>
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<tr>
<td>AMV Anion PS/butadiene</td>
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<td>1.9</td>
<td>0.14</td>
<td>19</td>
<td>2.0–4.5</td>
<td>92</td>
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<tr>
<td>HJC Cation heterogeneous</td>
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<td>1.8</td>
<td>0.83</td>
<td>51</td>
<td>–</td>
<td>–</td>
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<tr>
<td>61CZL386 Cation heterogeneous</td>
<td>Homogeneous</td>
<td>2.6</td>
<td>0.63</td>
<td>40</td>
<td>9</td>
<td>–</td>
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<td>103PZL183 Anion heterogeneous</td>
<td>Homogeneous</td>
<td>1.2</td>
<td>0.60</td>
<td>38</td>
<td>4.9</td>
<td>–</td>
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<tr>
<td>Nafion 117 Cation fluorinated</td>
<td>Homogeneous</td>
<td>0.90</td>
<td>0.20</td>
<td>16</td>
<td>1.5</td>
<td>97</td>
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<td>Nafion 901 Cation fluorinated</td>
<td>Homogeneous</td>
<td>1.1</td>
<td>0.4</td>
<td>5</td>
<td>3.8</td>
<td>96</td>
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<td><strong>RAI Research Corp., USA</strong></td>
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<tr>
<td>R-5010-H Cation LDPE</td>
<td>Homogeneous</td>
<td>0.9</td>
<td>0.24</td>
<td>20</td>
<td>8.0–12.0</td>
<td>95</td>
</tr>
<tr>
<td>R-5030-L Anion LDPE</td>
<td>Homogeneous</td>
<td>1.0</td>
<td>0.24</td>
<td>30</td>
<td>4.0–7.0</td>
<td>83</td>
</tr>
<tr>
<td>R-1010 Cation fluorinated</td>
<td>Homogeneous</td>
<td>1.2</td>
<td>0.10</td>
<td>20</td>
<td>0.2–0.4</td>
<td>86</td>
</tr>
<tr>
<td>R-1030 Anion fluorinated</td>
<td>Homogeneous</td>
<td>1.0</td>
<td>0.1</td>
<td>10</td>
<td>0.7–1.5</td>
<td>81</td>
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<tr>
<td>MA-40 Anion</td>
<td>Homogeneous</td>
<td>0.6</td>
<td>0.15</td>
<td>17</td>
<td>5.0</td>
<td>95</td>
</tr>
<tr>
<td><strong>CSMCR, Bhavnagar India</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>IPC Cation LDPE/HDPE</td>
<td>Homogeneous</td>
<td>1.4</td>
<td>0.14–0.16</td>
<td>25</td>
<td>1.5–2</td>
<td>97</td>
</tr>
<tr>
<td>IPA Anion LDPE/HDPE</td>
<td>Homogeneous</td>
<td>0.8–0.9</td>
<td>0.16–0.18</td>
<td>15</td>
<td>2.0–4.0</td>
<td>92</td>
</tr>
<tr>
<td>HGC Cation, PVC Heterogeneous</td>
<td>Homogeneous</td>
<td>0.67–0.77</td>
<td>0.22–0.25</td>
<td>14</td>
<td>4.0–6.0</td>
<td>87</td>
</tr>
<tr>
<td>HGA Anion, PVC Heterogeneous</td>
<td>Homogeneous</td>
<td>0.4–0.5</td>
<td>0.22–0.25</td>
<td>12</td>
<td>5.0–7.0</td>
<td>82</td>
</tr>
</tbody>
</table>

Measured: *0.5 M NaCl and **0.1/0.01 M NaCl at 25 °C.
All the intermediate forms are considered as the polymer blends from the viewpoint of macromolecular chemistry. As a consequence of the polymer/polymer incompatibility, on one hand, a phase separation of the different polymers is obtained, while on the other hand, a specific aggregation of the hydrophilic and hydrophobic properties of the electrolyte is obtained. A classification of the membrane morphology is then possible, depending on the type and size of the micro phase. The membranes are translucent, an indication that inhomogeneities, if any, are smaller than the wavelength of visible light (400 nm). Thus, these membranes are called interpolymer or micro-heterogeneous membranes.

### 2.1. Homogeneous ion-exchange membranes

The method used for the preparation of homogeneous ion-exchange membranes can be summarized in three different categories:

1. Polymerization or polycondensation of monomers; at least one of them must contain a moiety that either is or can be made anionic or cationic, respectively
2. Introduction of anionic or cationic moieties into a preformed solid film
3. Introduction of anionic or cationic moieties into a polymer, such as polysulfone, followed by the dissolving of the polymer and casting it into a film.

Monomers used for membranes preparation by polymerization or polycondensation should contain at least one of them and must contain a cationic or anionic moiety. For the polycondensation type of the membranes, formaldehyde is used as a cross-linking agent to make water insoluble membrane while use of suitable monomeric/polymeric material endowed with ion-exchange properties. The first membranes made by polycondensation followed by cross-linking with formaldehyde were prepared from phenolsulfonic acid [27]. Phenol was treated with concentrated sulfuric acid at 80 °C; which leads to the phenolsulfonic acid in para form, a brown crystalline material. This acid was then reacted with a 38% solution of formaldehyde in water initially at −5 °C for about 30 min and then at 85 °C for several hours. The solution was then cast into a film, which resulted cation-exchange membrane after cooling at room temperature. Excess monomer was removed by washing the film in the distilled water. With the slight modification of this procedure [19], condensation of anisole or sulfonated phenol with formaldehyde and subsequent casting the membrane on glass plate or mercury followed by curing at 90 °C resulted the cation-exchange membrane.

Similarly, anion-exchange membranes were prepared by condensation of M-phenylene diamine or aliphatic diamine compounds such as polyethylene diamine or diacylondiamine with formaldehyde. The resulting membranes exhibited good electrochemical properties but were lack in mechanical strength.

The perfluorinated membranes with high equivalent weights (EW) have limited applications in fuel cells because of their high cost and fuel loss. The Dow Chemical Company overcame this with the development of the low EW perfluorinated membranes in 1988. These membranes were prepared by the co-polymerization of tetrafluoroethylene with vinyl ether monomer as per scheme presented in Fig. 3. This polymeric structure can be described as a Teflon-like backbone with a side chain attached via an ether group, which is a terminal sulfonate functional group. The synthesis of the Dow epoxy (Fig. 3) [31] is more complicated than that of the Nafion epoxy (Fig. 2) [32]. Both types of membranes were commercialized [33]. A perflurinated ionomer membrane has also been developed by the Asahi Glass Company and

![Fig. 1. Reaction of phenol sulfphonic acid with formaldehyde.](image-url)
commercialized as Flemion. The general properties of the long-side-chain perfluorinated ionomer membranes (e.g. Nafion/Flemion/Aciplex) and the short-side-chain perfluorinated ionomer membranes (e.g. Dow) are as follows: a) EW range = 800–1500; b) conductivity = 0.20–0.05 S/cm² (for example, conductivity 1100 EW = 0.1 S/cm² and conductivity 850 EW = 0.15 S/cm²).

2.1.2. Styrene–divinylbenzene based membranes

Styrene–divinylbenzene based ion-exchange membranes are well reported in the literature for the application of the electrodialysis [34,35]. Membranes commercialized from Tokuyama Soda Co. (Neosepta) and Asahi Glass Co., are copolymer of styrene and divinylbenzene, followed by sulfonation and amination in solution or bulk gives the cation and anion-exchange membranes, respectively. Sulfonation of the polymer was achieved by chlorosulfonic acid or concentrated sulphuric acid in dichloroethane using the silversulfate as catalyst. The anion-exchange membrane was prepared by chloromethylation of the polymer followed by the amination. The reaction scheme for these membranes is shown in Fig. 4.

It is known [36] that for the pure styrene–divinylbenzene cation-exchange membrane, selectivity for the monovalent ion is poor with no remarkable effect of cross-linking agent on the selectivity of the particular cations. The mobility of the multivalent cations decreases with an increase in the cross-linking because of the compact membrane structure. For commercial application, special types of ion selective membranes were prepared using these monomers, such as monovalent ion selective for the production of table salt, high hydrogen ion retention to recover acids from the waste water, etc. The hydrogen ion can pass selectively through the membrane against all other ions in electrodialysis, thus the

\[
\text{The general structure of the Dow membrane: } x = 3-10; \ y = 1 \text{ and } z = 0
\]

\[
\text{Fig. 2. (a) Reaction scheme and (b) chemical structure of the Nafion membrane.}
\]

\[
\text{Fig. 3. Schematic reaction for the preparation of Dow membrane.}
\]
development of the membranes with high acid retention was really challenging for the application of the acid recovery. Sata [37,38] had carried out significant research work on the monovalent ion selective membranes for the application of production of the table salt from seawater. He has reported the surface modification of the membranes for enhancing relative permselectivity between ions with the same charge in electrodialysis [37,38]. He also proposed several mechanisms such as: sieving of the ions with variation of cross-linkage, effect of charge, and electrostatic repulsion, on permselectivity, and specific interaction between the ion-exchange groups in the membrane matrix and counter-ion. In the case of the anion-exchange membrane, the sieving of the ions by highly cross-linked layers was effective for changing the permselectivity between chloride and sulfate ions. Also sieving can be effective by introducing the dense polyelectrolyte layer on the membrane surface, like polymerization of the pyrrole on the surface of the cation and anion-exchange membranes to change the permselectivity for the larger ion, such as calcium and sulfate ion with respect to sodium and chloride ions, respectively. Selective permeation of specific ions is mainly dependent on the degree of the affinity of the specific anions with the anion-exchange membrane, and partially on the change in mobility through the membrane. The affinity of the specific ions to the membrane is depending on the balance of the hydrophilicity of the membrane, as done by introducing the polysaccharide layer made up of poly(N-dodecyl 4-vinylpyridine bromide) on the anion-exchange membrane interfaces. Utilization of electrostatic repulsion force to change the permselectivity has been studied from various aspects and effective on achieving monovalent cation and anion permselectivity [37,38]. It is reported that a bipolar ion-exchange membrane is selectively permeate to

![Reaction scheme for the preparation of styrene–divinylbenzene based ion-exchange membranes.](image-url)
lower valent cations compares to higher ones. Polyaniline composite styrene–divinylbenzene based membranes were also prepared and characterized in order to observe the selectivity of various mono- and bi-valent ions [5]. Results enable the understanding of the variation of the CEM/PANI or AEM/PANI composite membranes permselectivity for different type of counter-ions with polymerization time. Permselectivities for cations across CEM/PANI follow the trend $\text{Na}^+ > \text{Ca}^{2+} > \text{Cu}^{2+}$ while for anions across AEM/PANI follow the trend $\text{Cl}^- > \text{SO}_4^{2-}$. Frictional interpretation of experimental results also supports the blocking behavior of PANI on the ion-exchange membrane surface. Based on the interpretation models for CEM/PANI and AEM/PANI composite membranes were also proposed. Electro dialysis results also suggest very small dialytic rate or low migration of bi-valent electrolyte ($\text{Na}_2\text{SO}_4 > \text{CaCl}_2 > \text{CuCl}_2$) in the presence of NaCl. Thus these membranes will be very useful for the separation of different electrolytes by electro-driven membrane technology. Surface of these membranes was also modified by the radiation grafting of urathane acrylates in order to introduce antifouling characteristics [39].

2.1.3. Partially fluorinated ionomer membranes

The preparation of the monomer $\alpha,\beta,\beta$-trifluorostyrene was carried out by Cohen et al. [40] and also by Prober [41]. The structure of the polymer is shown in Fig. 5. Hogdon has investigated the sulfonation of $\alpha,\beta,\beta$-trifluorostyrene [42,43] and prepared a multiplicity of equivalent weight or different ion-exchange capacity of both linear and cross-linked poly-$\alpha,\beta,\beta$-trifluorostyrene sulfonic acids. He reported that difficulty in sulfonation of poly-$\alpha,\beta,\beta$-trifluorostyrene was observed because of the beta-directing influence of the perfluorinated polyalkyl group attached to the aromatic ring [42]. The degree of sulfonation was found to be dependent on the temperature and the concentration of the chlorosulfonic acid. The linear poly-$\alpha,\beta,\beta$-trifluorostyrene sulfonic acid was prepared by a direct combination of the chlorosulfonic acid with the trifluorostyrene. Sulfone cross-linked poly-$\alpha,\beta,\beta$-trifluorostyrene sulphonlic acid was also prepared. This type of material was found to be resistant to oxidative mode of degradation, which causes drastic oxidative depolymerization of the polystyrene and polystyrene–divinylbenzene sulfonic acids. This was attributed to the substitution of fluorine in the place of the benzyl-hydrogen atom of polystyrene leading to the added C–F bond strength required to resist the oxidation environment. It was claimed that the high stability of the fluorine atoms attached to the alkyl carbon atoms impacts oxidative and thermal stability superior to that exhibit by conventional ion-exchange polymers such as styrene sulfonic acid.

2.1.4. Polysulfone based ion-exchange membranes

For electrodialysis process under severe conditions such as high temperature and strongly oxidizing conditions, a more stable Nafion and Dow ion-exchange membranes have been developed and successfully applied under those conditions. However, it has found only a few major industrial applications, other than the chlor-alkali industry, primarily because of its high cost. So there has been a challenge to develop new types of ion-exchange membranes, which would be cheap but also have good electrochemical properties and excellent resistance to degradation by heat and chemical attack.

Engineering plastics such as polysulfone and polyethersulfone have been widely used as a base polymer for ultrafiltration and gas separation because of their excellent workability and mechanical strength [44–48]. Polysulfone membrane with excellent chemical resistance has been studied for its application as an ion-exchange membrane by improving the permeability for ultrafiltration and reverse osmosis, or imparting ion permselectivity by introducing ion-exchange groups into the membrane [49–51]. Several workers [52,53] had earlier prepared ion-exchange membranes using polysulfone as a base polymer of the membrane. The sulfonation procedure of the membranes was achieved either by the solution procedure [54] or by the slurry procedure [55] and their properties have been described [56,57]. The sulfonation procedures for poly(arylene ether sulphone) Udel P-1700 (PSU) and Vitrex PES 5200P (PES) is described in the patent literature [55,58] (Fig. 6).

An alternate sulphonation process for polysulfone PSU ionomers is also available in the literature [59–63]. It was reported that these polymers were cross-linked by a new cross-linking procedure. The basic working hypothesis for the new type of sulfonation method reported, sulfonation at the ortho position to the ether bridge of the bisphenol-A by electrophilic substitution [64]. This part of the molecule has a high electron density (+M effect from the ether bridge, +1 effect from the isopropylidine group), in contrast to the diarylsulfone portion of the monomer-repeating unit, with low electron-density due to the electron-withdrawing SO$_2$ group ($-I, -M$ effect). One disadvantage of electrophilically sulfonated poly(sulfone) is that the SO$_3$H group undergoes ipso-substitution with H$^+$, which lowers the hydrolytic stability of the sulfonated poly(sulfone) in strong acids. This limits the application of commonly sulfonated poly(sulfone) as a cation-exchange polymer in electro-membrane process.

Fig. 5. Structure of trifluorostyrene based membrane.

Fig. 6. Structure of Udel polysulfone.
The new method based on the sulfonation of polysulfone in the diarylsulfone part showed increased hydrolytic stability against ipso-substitution by H⁺, compared to electrophilically sulfonated polysulfone, due to the electron-deficit of the diarylsulfone position of the polymer. In the literature [63] it has been found that PSU Udel can be substituted in the electron deficient portion of the monomer repeating unit by first deprotonation of the aromatic ring position ortho to the sulfone bridge with metalorganic reagents and subsequent reaction of the metalated site with electrophiles. Deprotonation reactions by attack of metalorganics at polymer backbones are also known from poly(2,6-dimethyl-para-phenylene ether) (PPO), poly(styrene), poly(vinylthiophene) and poly(methylphenylphosphazene). To convert the metalated site of the deprotonated polymer into a sulfonic acid group, the metalated polymer is quenched with the electrophile SO₂, and the metal sulfinate derivative of the respective polymer. Sulfinates and particularly the corresponding sulfinic acids are known to be chemically unstable and can easily be oxidized to sulfonic acids.

Based on the aforementioned facts, a three-stage process has been developed for introduction of the sulfonic acid group in the diarylsulfone part of the poly(sulfone) Udel [64]. The scheme for this process is presented in Fig. 7. The sulfonation process consists of the following steps: a) lithiation of the polymer in a 2.4 wt.% THF solution with 10 N n-butyllithium, at temperature ranging from −50 to −80 °C under argon. The lithiation proceeds very fast (0.5 h) and nearly quantitative, as has been proved by NMR. b) Introduction of SO₂ into the reaction vessel containing the lithiated polymer at temperature from −65 to −20 °C. The reaction of the lithiated polymer with the electrophile SO₂ is also nearly quantitative as has been proved by ¹H NMR. The sulfonation reaction is finished after 5–10 min of SO₂ introduction. c) Oxidation of the formed sulfinate. Alkaline or neutral H₂O₂, sodiumhypochlorite, or KMnO₄ solutions were used to achieve the oxidation with aqueous solution or suspension after isolating the polymeric sulfinate. d) Conversion of the lithium sulfonate to the corresponding sulfonic acid by aqueous HCl (water insoluble polymeric sulfonic acids) or by stirring of the sulfonate with a cation-exchange resin (water-soluble polymeric sulfonic acid).

The ion-exchange capacity (IEC) of the resulting polymer largely depends on the oxidation step. A loss in sulfinate groups can partially be caused by splitting-off of the sulfinate group during the oxidation process and subsequent substitution by hydrogen (ipso reaction). However, by selection of the best suitable oxidation conditions the loss in IEC can be minimized, as oxidations of PSU-SO₂-25 with KMnO₄, where 98.9% yield of the oxidation products are obtained. At higher to medium degree of sulfination KMnO₄ and NaOCl are the most suitable oxidants (3.3–1.9 meq/g of IEC). For the low degree of sulfination, nonionic oxidant H₂O₂ should be used. The membrane swelling largely depends on the IEC. At IECs ≥ 2.4 2.4 meq/g dry polymer the polymer becomes water-soluble. The specific conductance of the membranes depends on the IEC and was lower than the Nafion membrane, which can be explained by stronger clustering of the SO₃H in Nafion because of its extremely hydrophobic backbone [65].

In another approach of sulfonation procedure for such polymers, modification of monomer makes feasible control of the molecular structures. Both biphenols and dibalides can be modified to incorporate functional groups or new monomers containing functional groups can be synthesized with the similar structure as their counterparts. Recently, Ueda et al. reported the sulfonation of 4,4’-dichlorodiphenylsulfone allowing two sulfonic acid groups per repeating unit [66]. Moreover, modified procedure for the preparation of highly sulfonated poly(arylene ether ketones) membrane via direct polymerization route is also reported, where the molecular weight and end groups have been controlled with the addition of monofunctional end capper [67]. The sulfonation of 4,4’-dichlorodiphenylsulfone had been carried out with power sulfonating agent (fuming sulfuric acid) and at relatively high temperature (100 °C). They were also investigated as potential new material for proton-exchange membranes.

It is reported that [68–70], the ion-exchange membranes prepared using polysulfone as a base polymer are likely to undergo a dimensional change during flocculation, which was responsible for the defects and change in ion-exchange capacity (IEC) because of high water affinity. Hence, it appears difficult to obtain a membrane having sufficient mechanical strength, and dimensional stability [71]. The water tends to concentrate in molecular clusters around the ionic groups and, therefore, the affinity of the membrane to water increases with IEC. The high water affinity leads to low cohesive forces, and a membrane swells quite strongly in water [68].

Terada et al. [72,73] have reported a new type of ion-exchange membrane using a block copolymer having segments, to which ion-exchange groups can be introduced readily. This type of membrane exhibited higher mechanical strength as compared to the others formed by segments, in which ion-exchange groups can hardly be introduced. The advantage of the block copolymer is that, the cohesive force of the part of polymer without ionic groups controls the swelling of the membrane. The anion-exchange membrane prepared by block copolymers of polysulfone (PS) and polyphenylenesulfidesulfone (PPSS) in the two steps: (i) chloromethylation of the polymer and (ii) amination of the chloromethylated copolymers [74]. These membranes showed good dimensional stability with poor electrochemical properties. Sulfonation of the copolymer with triethyl phosphate and sulfuric acid yields cation-exchange membrane with poor electrochemical properties [74]. Recently, Yang et al. reported [75] block copolymers of poly(vinylidene fluoride) with Bisphenol-A polysulfone by polycondensation of α,ω-dihydroxybisphenol-A poly(sulfone) precursors and α,ω-dibromopoly(vinylidene fluoride) [76]. Sulfonation of the block copolymer has been done by the post-sulfonation method using (CH₃)₃SiSO₃Cl as reported in Ref. [77]. In brief, trimethylsilyl chlorosulfonate was added to the polymer solution in chloroform, and mixture stirred for 24 h at room temperature. Excess of sodium methoxide was added in order to cleave the silyl sulfonate intermediate to obtain the sodium
sulfonate form, which was dissolved in the DMF and precipitated as its acidic forms in 2 M HCl.

2.1.5. Partially sulphonated poly(ether ether ketone) (PEEK) membranes

The electrophilic aromatic sulphonation of the poly(ether ether ketone) was reported in the literature [78]. The general concept of the sulphonation consists in dissolving the dried PEEK in concentrated sulphuric acid. The desired level of sulphonation depends on the time and temperature of the reaction. As an example, Bailey et al. [79] have sulphonated the PEEK by dissolving 10 g of oven dried PEEK in 100 ml of 96% H2SO4. The time and temperature of the deep red viscous solution were varied in order to achieve the desired level of sulphonation. The reaction was quenched by slowly pouring the acidic solution into 1 l of distilled water. The precipitation of the polymer may appear instantly forming a continuous string. In the last step, the polymer was extensively washed to remove the excess acid, and dried in a vacuum oven at 100 °C [78].

Unfortunately, these membranes have swollen in a gel-like state, which make them mechanically very fragile with limited lifetime in electrolysis system. There are different strategies for reduction of swelling of the ion-exchange membranes, which include cross-linking the polymer with suitable cross-linking agent, blending the polymer, which are capable of formation of hydrogen bonds. The formations of hydrogen bonds lead to compatibilization of the blend polymers. Many examples of this type of blends are mentioned in the literature [80]. Cui et al. [81] developed blend ion-exchange polymer membranes by blending of sulfonated poly(ether ether ketone) (SPEEK) with aminated PSU Udel (PSU-NH2), polyamide PA 6-3-T (Trogamid P) (Huls), and poly(etherimine) PEI Ultem (General Electrical). For the blend membrane swelling was reduced by specific interactions either between PA and PEI hydrogen bonds, or between PSU-NH2 (partial) polysalt, leading to electrostatic interaction or hydrogen bonding between the blend component of macromolecules, the acid–base interactions also led to decrease of ionic conductivity by partial blocking of SO3\(^-\) groups for cation transport, compared with the ionic conductivity of the hydrogen bond blends. The acid–base blends showed better ion permselectivities than the hydrogen bond blends, even at high electrolyte concentrations, and thus better performance in electrodialysis. The thermal stability of the blends is good and in the case of acid–base blend it was even better. The investigated blend membranes showed similar performance as the commercial cation-exchange membrane in electrodialysis application. The performance of the acid–base blend membrane is better than the hydrogen bonded PEEK-PA blend membrane, especially in the ED experiment at higher NaCl concentration. This may be due to lower swelling and thus higher permselectivity of the acid–base blend membranes compared with the PEEK-PA blend.

2.1.6. Polybenzimidazole based ion-exchange membranes

Polybenzimidazole were synthesized from aromatic bis-o-diamine and dicarboxylates (acids, esters, amides), either in the molten state or in solution. The thermal stability of these materials depends on the nature of the component tetradiamine and dicarboxylate acids have been largely reported in the early literature [82,83]. Aromatic polybenzimidazoles are highly stable, with melting point 600 °C. The commercially available polybenzimidazole is poly-[2,2-(m-phenylene)-5,5'-bibenzimidazole], which was synthesized from diphenyl-iso-phthalate and tetraaminobiphenyl (PBI). It was characterized with the excellent thermal and mechanical stability. Linkose [84] observed no weight gain/loss for PBI in either H2/H2O or O2/H2O at 200 °C, although its stability at 300 °C in oxidizing condition was not satisfactory. It was concluded that at 300 °C, the imidazole ring is susceptible to hydrolysis, and that the product of this hydrolysis is more readily oxidizable. Functionalization of PBI can be obtained by the abstraction of the hydrogen from –NH-group and then grafting of the functional group on the anionic PBI polymer backbone [85].

2.1.7. Polyimide based ion-exchange membrane

Due to the thermal, mechanically stable and chemically resistant nature of polyimide, it leads to an alternative membrane forming material for electro-driven process [86,87]. Various structures of sulfonated polyimide (SPI) materials were recently studied [88–92]. Genies et al. [86] synthesized SPI membranes with random and sequence.
polymers but did not achieve the high proton conductivity enough for the practical application. Sulfonated polyimides based on 4,4-diamino-biphenyl 2,20-disulphonic acid (BDSA), 4,4-oxodianiline (ODA) and oxy-diphthalic anhydride (ODPA) was the first commercially available polyimide. These polymers called phthalic polyimides were soluble in m-cresol and were unstable in fuel cell conditions[88]. A second generation sulfonated polyimides based on 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) instead of ODPA were investigated. Swelling measurements, ionic conductivity and fuel cell experiments were performed on these membranes [88], which showed that naphthalenic SPIs are promising materials for PEMFC. Unfortunately, their solubility was greatly reduced compared to phthalic SPIs since they are soluble in chlorophenol.

2.1.8. Polyphosphazene ion-exchange membranes

Polyphosphazenes are the new class of base-polymers for ion-exchange membranes because of their thermal and chemical stabilities, and the ease of chemically altering the polymer by adding various side chains onto the –P≡N-backbone. Sulfonated polyphosphazene cation-exchange membranes, may be an attractive alternative to perfluorosulfonic acid and polystyrene sulfonate membranes. However, there are few reports available in the literature on the preparation and characterization of sulfonated polyphosphazenes ion-exchange membranes. The difficulty associated with producing such membranes lies in preparing the sulfonated polyphosphazene and balancing the hydrophilicity of the resulting polymer to prevent dissolution in aqueous solution [93]. One of the main methods used for the synthesis of these polymers is illustrated in Fig. 8. Poly(dichlorophosphazene) reacts with a wide variety of nucleophiles and yields high molecular weight organic-derivatized polymers with properties that vary widely with the side group structure. The stability of the phosphorus–nitrogen backbone makes this class of macromolecules suitable for the surface modifications. Alcock et al. [94] reported that the molecular level and surface sulfonation of aryloxy- and (arylamino) phosphazene was accomplished through the use of concentrated sulfuric acid. He also reported [95] the sulfonation of aminophosphazene with 1,3-propanesulfone, but the reaction yields were very low. Monotoneri et al. [96] showed that (Aryloxy) polyphosphazene also could be sulfonated via the use of sulphur trioxide. The sulfonation of poly[bis(phenoxy)phosphazene] in dichloromethane with SO₃ was also achieved [96], with mole ratio of SO₃ to phosphazene less than one. There was no C-sulfonation and up to 50% of the nitrogen skeleton were attacked and formed :=N→SO₃ complex. For SO₃/polyphosphazene with molar ratios greater than one, C-sulphonation was observed, mainly at the meta-position in the phenoxy side groups.

 Usually, sulfonation of polyphosphazene yields water-soluble polymers [93]. In practice, water insoluble sulfonic acid membranes from polyphosphazene polymers can be made, by the cross-linking of polyphosphazene membranes followed heterogeneous sulfonation [97]. Also homogeneous or heterogeneous polymer sulfonation was carried out, followed by film casting and cross-linking. These two methods require that the polyphosphazene contain side groups that can be used for cross-linking or in the second case; sulfonate groups can serve this purpose [98]. The water insoluble polyphosphazene can be made by introducing the alkyl groups on the phenoxy ring followed by controlling mole ratio of sulphonating agent to polyphosphazene mole ratios [99].

2.1.9. Styrene/ethylene-butadiene/styrene triblock copolymers

Styrene/ethylene-butadiene/styrene triblock polymer is a commercially available product (Kraton G1650) containing a saturated carbon center block, which is inert to the sulphonation reaction. AMV anion-exchange membranes commercialized by Asahi Glass Co belong to this category. This polymer has good mechanical and chemical stability [100–102]. The typical casting solvent of the sulfonation process is reach in n-propanol, which should preferentially solvate the sulfonated styrene blocks. It has been claimed that membranes with reproducible properties at a constant sulfonation were obtained. Membrane conductivities at sulfonation levels above 50 mol% of styrene units exceed that of Nafion under similar measurement conditions. In particular, a sulfonation level of 60% was found to be a good balance of electrical and mechanical properties.

2.1.10. Ion-exchange membranes by the sol–gel method

Nanostructured organic–inorganic composite materials [103–113] are currently objecting tremendous research because of their versatile properties of mechanical stable inorganic backbone and the specific chemical reactivity of the organo-functional group. These interesting properties of
new materials were dependent on their structural and chemical composition as well as on the dynamical properties inside the blend. Sol–gel process makes possible a relatively easy incorporation of pure inorganic phase into an organic matrix. A low temperature procedure, high purity of reactants and possibility of mixing of precursors of organic and inorganic phases on molecular level are the main advantage of this technique [103].

Basically, sols are dispersions of colloidal particles (size 1–100 nm) in a liquid and a gel is an interconnected, rigid network with pores of sub micrometer dimensions and polymeric chains whose average length is greater than a micron. In the sol–gel process the reaction of Si(OR)4 occurs as follows.

\[
\text{Si(OR)}_4 + \text{H}_2\text{O} \rightarrow \text{Si(OR)}_3\text{(OH)} + \text{ROH}
\]

Intermediates due to the partial hydrolysis include molecules with Si–OH groups, and these are called silanols. Complete hydrolysis to form Si(OH)4 would yield silicic acid, but is difficult to achieve. Instead, condensation may occur between either two silanols or a silanol and an ethoxy group to form a bridging oxygen and a water or ethanol molecule. An example of a condensation reaction between two silanols with the elimination of water is shown below.

\[
\text{Si(OR)}_4 + \text{Si(OR)}_3\text{(OH)} \rightarrow \text{(OR)}_3\text{SiOSi(OR)}_3\text{(OH)} + \text{H}_2\text{O}
\]

Then hydrolysis of (RO)4 SiOSi(OR)3 resulted (RO)2 Si(OH)OSi(OR)3, which can undergo further polymerization reactions. The hydrolysis and polycondensation reactions are initiated at numerous sites and the kinetics of the reactions is therefore complex. When a sufficient number of interconnected Si–O–Si bonds are formed in a region, they interact cooperatively to form colloidal particles or a sol. With time, the colloidal particles link together to form a three-dimensional network. At gelation, the viscosity of the solution increases dramatically and a solid object termed an alcogel results. A technologically important point is that alcogels can be formed in any shape or desired configuration. SiO2 alcogels prepared by Hench and West and Kurumada et al. [103,104], acid or base catalyzed processes lead to gels with vastly different structures and morphologies. Acid-catalysis forms linear polymers, which are weakly cross-linked. These polymers entangle and form additional branches, resulting in gelation, whereas, base-catalysis forms more highly branched clusters due to more rapid hydrolysis [110]. Gelation occurs by linking of the clusters. Both catalyzed reactions are bimolecular nucleophilic substitution reactions. The acid catalyzed mechanisms are preceded by rapid protonation of the OR or OH substituents bonded directly to silicon atom, whereas under basic conditions hydroxyl or silanol anions attack silicon atom directly. The possible mechanism for both acid and base catalyzed reactions can be shown in Fig 9.

Sol–gel derived silicon oxide networks, under acid-catalyzed conditions, yield primarily linear or randomly branched polymer [103,104], which entangle and form additional branches resulting in gelation as shown in Fig. 10(a). However, silicon oxide networks derived under base-catalyzed conditions yield more highly branched clusters, which do not interpenetrate prior to gelation and thus behave as discrete clusters as shown in Fig. 10(b).

It is reported that [106,107] higher ion-exchange capacity, permselectivity and conductivity for acid catalyzed hybrid membranes than the base catalyzed membranes were obtained with the same composition, which indicated that former route is suitable for the preparation of ion-exchange membranes. But for the heterogeneous membrane [105] preparation extent of resin loading was the maximum with the base catalyzed membranes which may be due to the cluster formation in the hybrid matrix.

A cation-exchange membrane based on poly(benzylsulfonic acid) siloxane (PBSS) was obtained by sol–gel process after different steps. It was based on the hydrolysis condensation of the benzyl–triethoxysilane precursor in a methanol solution containing water and triflic acid (F₃SO₃H). The steps of preparation are indicated elsewhere [114,115] and their structure is shown in Fig. 11. The polymer was sulphonated in dichloromethane solvent using chlorosulfonic acid. Several co-polymer compositions prepared from different proportions of the mixture of benzyl–triethoxysilane, n-hexyl trimethoxysilane and ethoxysilane (e.g. different organically modified alkoxysilanes). Cross-linking was also performed in THF by hydrosilylation of silane groups with divinylbenzene using divinyltetramethylsiloxane platinum complex as catalyst. These membranes were thermally stable up to 250 °C. A conductivity of 1.6 × 10⁻² Ω⁻¹ cm⁻¹ at room temperature [114] was observed.

A new series of positively and negatively charged ion-exchange membranes has been prepared using sol–gel method with acid catalyzed hydrolysis condensation of the silica precursors by the Cuiming et al. [111,112]. The hybrid membrane was prepared from trimethoxysilyl functionalized polyethylene oxide and quaternized with ethyl bromide. The trimethoxysilyl functionalized polyethylene oxide was obtained by endcapping polyethylene oxide with toluene 2,4-disocyanate, followed by the reaction with N-[3-(trimethoxysilyl) propyl] ethylene amine. Kogure et al. [113] reported that ethylpyridine–trimethoxysilane or [Me₃N⁺(CH₂)₃–Si(O–Me)₃]Cl was used as precursors for sol–gel process. Since they are silane-coupling agents of relatively low molecular weight, it is hard to obtain hybrid materials with high organic component.

Organic–inorganic composite anion-exchange membranes based on PVA–SiO₂ were also prepared by aqueous dispersion polymerization (sol–gel) method and anion selectivity was introduced in the membrane matrix by the chemical grafting of 4-vinyl pyridine (4-VP) with desired content. In all these composite membranes, inorganic content is fixed, which
contributes towards the reduction of swelling properties of PVA, while 4-VP, which is essential for the introduction of ionogenic functional groups contributes towards the increase in the swelling properties of the membrane matrix [116].

2.2. Heterogeneous ion-exchange membranes

Ion-exchange membranes, both the homogeneous and heterogeneous, being unique in their nature overcome each other in one way or another. Homogeneous membranes having good electrochemical properties lack in their mechanical strength, whereas heterogeneous membranes having very good mechanical strength are comparatively poor in their electrochemical performance [117]. However, by choosing a suitable binder to make non-reinforced membranes or by choosing a suitable reinforcing fabric, it is possible to have good ion-exchange membranes by an optimum combination of electrochemical properties and mechanical strength with heterogeneous method. Ion-exchange membranes commercialized by Ionics Inc., USA; HGC and HGA membranes developed by CSMCRI, Bhavanagar, India belong to this category.

Heterogeneous ion-exchange membranes can also be made by mechanical incorporation of powered ion-exchange resin into sheets of rubber, PVC, acrylonitrile copolymers or some other extrudable or mouldable matrix. Such membranes can be prepared [118] either by (i) calendaring ion-exchange particles into an inert plastic film or (ii) dry moulding of inert film forming polymers and ion-exchange particles and then milling the mould stock or (iii) resin particles can be dispersed in a solution containing a film forming binder and then the solvent is evaporated to give ion-exchange membrane [105]. Such heterogeneous membranes may also be reinforced with a chemically resistance fabric [119].

Vyas et al. [117] found that the particle size distribution of the resin particles of different mesh affected the electrochemical and mechanical properties of the membranes. It was observed that with increase in resin loading the membranes became more and more brittle, while the finer the resin particles, the more flexible was the membrane. It was found that, for PVC binder, with resin particles of –300 + 400 mesh (39 μm), it is possible to obtain flexible membranes up to 60% resin loading whereas the membranes become brittle even with 40% loading for
and ion-exchange capacity increases with decreasing the particle size. Decrease in the particle size results the higher surface area of the resin particles and thus the number of functional groups may actively participate in the transport of counter ions through the membrane, which results in lower resistance, and higher ion-exchange capacity.

2.3. Interpenetrating network (IPN) polymer ion-exchange membranes

IPN based ion-exchange membranes reported in the literature [120–122], possess an excellent combination of both electro-chemical and mechanical properties. Ion-exchange membranes commercialized by RAI Research Corp., USA; and IPC and IPA membranes developed by CSMCRI, Bhavnagar, India belong to this category. For the preparation of IPN membrane, linear polyethylene was used as a binder. It was made into an organosol with suitable solvating monomers like styrene – divinylbenzene. This blend, on polymerization of monomers under a free radical mechanism yields a chemical polyblend of two interpenetrating networks of linear and cross-linked polymer molecules [120,122]. In addition, due to grafting there may be an inter cross-linking between polyethylene and polystyrene phase. Such a chemical polyblend behaves like a homogeneous type having less probability of micro-voids compare to heterogeneous type membranes. For lack of such available space, when there is solvation of ionic groups, there is an expansion of matrix with attendant dimensional changes.

Recently [123] semi-interpenetrating polymer networks (s-IPNs) based ion-exchange membranes were prepared by mixing two polymers, polyvinyl alcohol, which is having the film forming property, and polyelectrolytes, followed by gaseous cross-linking with dibromoethane. The polyelectrolytes used to develop tailor-made cation-exchange membranes are, poly(sodium styrenesulfonate) (PSSNa), poly(styrenesulfonic acid) (PSSH), and poly(acrylic acid) (PAA). Also, poly(ethyleneimine) (PEI), poly(diallyldimethylammonium chloride) (PDDMACl), and poly(1,1-dimethyl-3,5-dimethylenepiperidinium chloride) (PDDPCI) were used for the preparation of anion-exchange membranes. With 60/40-mass ratio of poly(vinyl alcohol) (PVA) to polyelectrolyte, the homogenous film with suitable mechanical property was obtained. The membranes PVA/PAA show less swelling and less ion-exchange capacity compare to the PVA/PSSNa and PVA/PSSH membranes. The anion-exchange membranes prepared using the above polyelectrolytes are weak ion-exchange membranes.

Fig. 10. (a) Acid catalyzed: primarily linear or randomly branched polymer. (b) Base catalyzed: highly branched polymer clusters.

Fig. 11. Structure of poly(benzylsulfonic acid) siloxane based membrane.
In special type of anion-exchange membrane [124–127], synergistic effect of the change in ion-exchange equilibrium constants of various anions to chloride ions and the change in the ratio of mobility between anions have been studied, by developing membranes from the poly(vinyl alcohol), β-cyclodextrin and poly(N-ethyl 4-vinylpyridinium bromide) by the casting method, following the cross-linking reaction with formaldehyde. The cyclodextrin is the naturally occurring cyclic oligosacharides, mostly consist of six, seven and eight D-glucose unite for α-, β- and γ-cyclodextrin, respectively. The doughnut-shaped cyclodextrin has an interior cavity with a diameter of 4.7–5.3 Å (α-CD), 6.0–6.5 Å (β-CD) or 7.5–8.3 Å (γ-CD) [124]. They have a unique configuration, which makes the outer surface hydrophilic and the inner surface hydrophobic in nature. Because of the presence of hydrophilic outer surface and hydrophobic inner cavity, it was expected that the permeation of different anions through the anion-exchange membrane would be different. On the other hand, it was reported that the permselectivity of anions through anion-exchange membranes in the electrodialysis is governed by a balance of the hydrophilicity of anion-exchange membranes with the hydration energy of anions in permeating through the membrane [124]. β-cyclodextrin makes the membrane hydrophilic, in which the water content of the membranes increased with the increase in the content of β-cyclodextrin. Consequently, the transport numbers of less hydrated anions, nitrate and bromide ions, relative to chloride ions decreased and those of strongly hydrated anions, sulfate and fluoride ions, increased with increasing content of β-cyclodextrin.

In the US Patent [128], the semi-interpenetrating network of polyacrylonitrile with polyepichlorohydrine, followed by amination with 1-benzyl-1-azonia-4-aza-bicyclo [2,2,2]-octane hydroxide gives the anion-exchange membrane with good electrochemical and mechanical properties.

2.4. Membranes prepared by the grafting method

Radiation grafting of polymers is a well-known technique for the surface modification of the polymers, which affects their physical and chemical properties [129–134]. Irradiation of polymers by means of ionizing radiation such as γ-rays induces the formation of radicals on the polymers, polymer main chain from which polymerization of another monomer can be initiated. Therefore this technique makes it possible to bring together two highly incompatible polymers in one material having combined properties. In recent years large amount of efforts has been devoted for the use of this technique for the preparation of various types of membranes, because it controls the membrane composition and properties by proper selection of the degree of grafting. Moreover, it overcomes the membrane shaping problem where grafting can be started with a film in a membrane form. A number of papers published on radiation grafting of monomers onto polymers films to obtain ionomers for versatile applications, they are used as an anion and cation-exchange membranes in electrodialysis processes, water desalination, carrier for immobilization of medical products, separators in alkaline batteries, etc.

The ion-exchange membranes were made using polyethylene sheets by the grafting method followed by sulfochlorination and amination which have low electrical resistance combined with high permselectivity and excellent mechanical strength. The reaction scheme for the preparation of these membranes is shown in Fig. 12. Nasef et al. [133] prepared the proton-exchange membrane by simultaneous irradiation of γ-
rays from a $^{60}\text{Co}$ source at a dose rate of 1.32–15 kGy/h for grafting of styrene onto tetrafluoroethylene-co-hexafluoropropylene films at room temperature and cation-exchange membranes with sulfonic acid functionality by radiation grafting of styrene onto poly(tetrafluoroethylene-co-perfluorovinyl ether) (PFA) films using simultaneous irradiation followed by sulfonation reaction. The content of the polystyrene in the membrane was found to be strongly dependent upon the grafting conditions i.e. nature of the solvent, dose rate, irradiation time, monomer concentration, etc. Similar behavior was also obtained upon grafting of other monomers such as acrylic acid onto FET films and for grafting of styrene onto FEP films by preirradiation. It was found that the grafted FEP films possessed good mechanical stability, which encourages their use for the preparation of proton-exchange membranes.

Kostov et al. [129–131] showed the similar effect of irradiation dose on the anion-exchange membrane prepared by grafting of 4-VP onto low-density polyethylene (LDPE) and polytetrafluoroethylene (PTFE) films by irradiation from $^{60}\text{Co}$ $\gamma$-source or high-energy electron beam. The initial properties of the polymer i.e., mechanical strength, thermal and chemical resistance combined with ion-exchange properties of grafted polymer give valuable properties of the polymer. By varying the reaction conditions of the radiation copolymerization, grafted copolymers were obtained with 17.1% to 74.5% degree of grafting for LDPE and 0.7 to 13.4 for PTFE. The method of multiple grafting was used, involving postpolymerization effect, which provides possibility for the monomer to penetrate into the polymer matrix together with the stepwise generation of free radicals. He observed linear dependences of the irradiation dose on grafting degree for both films. Irradiation exerts stronger effect on the grafting on PTFE compared with that on LDPE, which is connected with the lower radiation resistance of C–F compared with C–H bonds. The water content of the membrane increases linearly with the grafting degree of 4-VP. The thickness of the grafted layer of the poly 4-VP affects the value of the specific resistance, which decreases with increase in the amount of grafted poly 4-VP. The transport number was found to be highest for the membrane between 5% and 25% degree of grafting.

2.5. Development of the bipolar membranes

Bipolar membranes have recently gained increasing attention as efficient tool for the production of acids and bases from their corresponding salts by electrically enforced accelerated water dissociation. Thus, they are a special type of layered ion-exchange membrane, consist of two polymer layers carrying fixed charges where one is only permeable for the anions and the other only for cations.

Bipolar membranes can be prepared by simply laminating conventional cation- and anion-exchange membranes. The total potential drops depend on the applied current density, the resistance of the two membranes and solution resistance. Since the specific resistance of deionized water is very high, the distance between the membranes of opposite polarity should be as low as possible. Laminated bipolar membranes often exhibit an unsatisfactory chemical stability at high pH values and rather poor water splitting capability and high electrical resistance. But special surface treatment of commercial ion-exchange membranes and subsequent laminating may also yield bipolar membranes with satisfactory properties. To minimize the electrical resistance, the thickness of the interphase between the oppositely charged membranes should preferably be less than 5 nm. It could also be shown that in bipolar membrane, the chemical stability is determined to a large extent by the properties of the positively charged anion-exchange moieties and by the properties of the matrix polymer. Furthermore, in practical applications bipolar membranes should not only have good chemical stability but also adequate water splitting capability.

In earlier days, bipolar membranes were prepared by coating layer by layer of the polymer with both functionalities. The materials mostly used for the ion selective layers of such bipolar membranes are the same as used for the preparation of anion or cation-exchange membranes, separately. Heterogeneous layers incorporate highly cross-linked ion-exchange particles in a film-forming polymer in both layers [135,136], or in the cation selective layer only [137,138]. Poly-vinylchloride (PVC) was used as film-forming polymer [136]. However, more recently base-stable polymers have been used such as poly-vinylidene fluoride (PVDF) [137], poly(sulfone) (PS) [138], or poly(ether sulfone) (PES). Another heterogeneous type of membrane has layers prepared from a porous, preformed polyethylene (PE) membrane that is soaked with the precursors of the ion-exchange polymer, i.e., styrene and divinylbenzene [139], being fictionalized in consecutive steps during membrane preparation. Various materials were used for preparing homogeneous bipolar membrane layers. Some are prepared from cross-linked styrene–divinylbenzene copolymers [140] similar to ion-exchange resins. After the cross-linking, each polymer layer becomes insoluble and the next layer can be applied on it. When solutions of non-cross-linked polymers, such as sulfonated poly-ether-sulfone (PES) was used for the cation selective layer and chloromethylated PES as precursor for the anion-exchange layer, the solvent of the second layer should be a non-solvent for the material of the first layer [141]. In this case solvent selection is a difficult task for some polymer combinations. More often, a homogeneous layer was cast from solution as the second layer on a preformed film that either has been cross-linked [142–145] or is of heterogeneous nature, i.e., contains ion-exchange particles in a non-conducting matrix polymer [137,138]. Both, the presence of cross-linking agents or heterogeneous materials in one or both layers of a bipolar membrane usually result in bipolar membranes with higher mechanical stability. Homogeneous membranes without such inherent stabilization require the use of additional reinforcement, such as woven cloths [145,146]. Apart from the base polymers, the nature of the charged groups that carry the ion-exchange functionality determines the transport behavior of an ion-exchange membrane, for two reasons: first, the charged groups in most common membranes are the same—the sulfonic acid groups provide the fixed negative charge of the cation permeable layers and quaternary
amine groups carry the positive charge in the anion permeable layers. These groups are permanently dissociated over almost the entire pH range and allow for a high conductivity of the ion selective layers. Second, many other ion-exchange groups are not completely dissociated into a fixed charge and a mobile ion over a wide pH-range. It has been found that such “weak” ion-exchange groups show catalytic activity for the water dissociation reaction. Examples for weak cation-exchange groups are the carboxylic acid or the phosphoric acid groups; weak anion-exchange groups are tertiary and secondary amines. Such materials are used in the contact region to enhance the water dissociation reaction in the electric field as discussed in the following section.

3. Characterizations of ion-exchange membranes

In an ion-exchange membrane, the fixed anions are in electrical equilibrium with mobile cations in the interstices of the polymer. In contrast, the mobile anions, called co-ions, are more or less completely excluded from the polymer matrix because of their electrical charge, which is identical to that of the fixed ions. This type of exclusion is called Donnan-exclusion in the honor of his pioneer work [147]. Due to the exclusion of co-ions, a cation-exchange membrane permits transfer of cations only. Anion-exchange membranes carry positive charges fixed on the polymer matrix. Therefore, they exclude all cations and are permeable to anions only. Thus the selectivity of ion-exchange membrane results from the exclusion of co-ions from the membrane phase. The Donnan-exclusion and thus membrane selectivity depend on: (1) the concentration of the fixed ions; (2) the valence of co-ions; (3) the valence of counter-ions; (4) the concentration of the electrolyte solution; and (5) the affinity of the exchanger with respect to the counter-ions.

Additional important parameters for the characterization of ion-exchange membranes are the density of the polymer network, hydrophobic and hydrophilic properties of the matrix polymer, charge density, membrane conductivity, and their morphology. It is difficult to optimize the properties of ion-exchange membranes because the parameters determining different properties often have opposing effects. For instance, a high degree of cross-linking improves the mechanical strength of the membrane but also increases in electrical resistance. The properties of ion-exchange membranes are determined by two parameters, namely the basic polymer matrix and the nature and concentration of fixed ion moiety. The basic polymer matrix determines to a large extent the mechanical, chemical and thermal stability of the membrane, while the concentration of the fixed ionic charges determine the permselectivity and electrical resistance of the membrane but they also have significant effect on the mechanical properties on the membrane [148–151].

3.1. Mechanical properties of the ion-exchange membranes

The mechanical characterization of ion-exchange membranes includes the determination of thickness, swelling, dimensional stability, tensile strength and hydraulic permeability. All tests should be carried out with pretreated and well-equilibrated membranes. Hydraulic permeability measurements provide information on the transport of components through a membrane under a hydrostatic pressure driving forces. The presence of pinholes in ion-exchange membranes will not only lead to a drastically increased hydraulic permeability but also invalidate any application. Pinholes can be determined by placing a wet membrane sheet on a sheet of white absorbent paper. 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 has to be spread over the entire surface. If no spot of the dye can be observed on the paper, the membrane is free of pinholes and can be tested for its hydraulic permeability. The test is carried out at room temperature using deionized water and a hydrostatic pressure driving force. The permeability can be calculated from the volumetric flow rate.

The swelling capacity of a membrane determines not only its dimensional stability but also affects its selectivity, electrical resistance and hydraulic permeability. It depends on the nature of the polymeric material, the ion-exchange capacity and the cross-linking density [149–151]. Usually the swelling of a membrane is expressed in turn of water content or uptake under given experimental conditions and can be defined by weight difference between the wet and dry membrane. A sample is equilibrated in deionized water, after removing the surface water from the sample the wet weight of the swollen membrane is determined. Then the sample is dried at elevated temperature until a constant weight is obtained. The water uptake is determined as weight percentage from the weight of the dry and wet sample. Water content in terms of water concentration in the membrane phase can be determined by means of the following equation [152,153]:

\[ C_w = \left( \frac{W_h - W_d}{\rho_w} \right) \frac{1}{M_w} \]

(1)

where \( C_w \) designates the concentration of water in the membrane, \( W_h \) the wet membrane weight, \( W_d \) the dry membrane weight, \( \rho_w \) the density of wet membrane and \( M_w \) the molar mass of water (18 g mol\(^{-1}\)).

The membrane porosity \( \tau \) (volume of free water within membrane per unit volume of wet membrane) can be obtained by following equation [116]:

\[ \tau = \frac{\Delta V}{(1 + \Delta V)} \]

(2)

where \( \Delta V \) designates the volume increase of the membrane upon absorption of the water per unit of dry membrane volume, which may be estimated by using following equation:

\[ \Delta V = \left( \frac{W_h - W_d}{\rho_d} \right) \rho_w W_d \]

(3)

where \( \rho_d \) is the density of dry membrane and \( \rho_w \) is the density of water, which enters into the membrane.

3.2. Chemical stability of membranes

The economics of electro-membrane processes is determined to a large extent by the chemical stability and the life of the ion-exchange membranes under applied conditions. Dete-
ioration in polymer matrix or functionality of the ion-exchange membranes after exposure for certain time periods to various test solutions containing acids, bases, or oxidizing agents is estimated by visual comparison with new, unexposed samples and by determining changes in their mechanical, dimensional and electrical properties.

3.3. Determination of membrane ion-exchange capacities

The ion-exchange capacities of charged membranes are determined by titrating the fixed ions, e.g. –SO₃⁻ or –R4N⁺ group with 0.1 N NaOH or HCl, respectively. For these tests, cation- and anion-exchange membranes are equilibrated for about 6 h in 1 N HCl or NaOH, respectively. The samples are then dried, and the ion-exchange capacity (EC; meq/g) of the membrane is calculated by [7],

\[ E_C = \frac{ab}{w} \]  

where \( a \) is the burette reading of acid, base or silver nitrate, \( b \) is the concentration of acid, base or silver nitrate and \( w \) is the dry weight of the membrane (g).

Further more, ion-exchange capacity can be used for the determination of fixed-ion concentration \( (X^m) \) of the membrane in units of (moles of sites) / (unit volume of wet membrane) by Eq. (5),

\[ X^m = \frac{\tau (IEC) \rho_d}{\Delta V} \]  

where IEC is expressed in equiv/g of dry membrane and \( \tau \) and \( \rho_d \) expressed in Eqs. (2) and (3).

3.4. Permselectivity

Ion selectivity of ion-exchange membrane is quantitatively expressed in terms of membrane permselectivity, which measures the ease with which counter-ion migration occurs through an ion-exchange membrane, and is defined as [154–156],

\[ P_S = \frac{f^{m}_i}{t_i} \frac{1 - t_i}{1 - t_i} \]  

where, \( P_S \) is the permselectivity of the membrane, \( f^{m}_i \) is the counter-ion transport number through the membrane, and \( t_i \) is the counter-ion transport number in the solution phase. Thus, the permselectivity of an ion-exchange membrane relates the transport of electric charge by specific counter ions to the total transport of electric charge through the membrane. An ideal permselective cation-exchange membrane would transmit positively charge ions only. The permselectivity approaches zero when the transference number within the membrane is identical to that in the electrolyte solution. Due to the Donnan exclusion the permselectivity of the membrane depends on the concentration of the electrolytes in the solution and on the ion-exchange capacity of the membrane. When a membrane separates dilute and concentration solutions, there will be concentration gradient across the membrane. In this case the permselectivity can be calculated by measuring counter-ion transport number across the ion-exchange membrane.

Transport number is determined by the Hiotf’s method [6,37,38] where increasing the concentration of certain ions in the feed and the decrease in the dilute solution were measured and by passing known amount of current trough the unit during the electrodialysis. A faster method for the determination of apparent permselectivities is based on membrane potential measurement. The experimental set-up for the membrane potential measurement is shown in Fig. 13.

The advantage of the determination of the potential between two solutions of different concentrations is that the tests are not obscured by concentration polarization effect at the membrane surface. The potential difference between two solutions of the same electrolyte but different concentration can be derived from the general flux equation and for the boundary conditions \( \Delta P=0 \) and \( J=0 \) (i.e. \( \sum_{z} zFJ_z = 0 \)). By introducing several approximations, such as negligible osmotic flow between the two solutions, constant ion mobilities and small concentration gradients across the membrane phase etc., according to TMS theory, the potential difference between solutions can be expressed for a monovalent electrolyte by Eq. (7) [157–159],

\[ E^m = \left(1 - 2f^{m}_i\right) \frac{RT}{F} \ln \frac{a_1}{a_2} \]  

Where \( E^m \) is the potential difference between two solutions containing a monovalent electrolyte, \( f^{m}_i \) the transport number, \( a_1 \) and \( a_2 \) are activities of electrolyte solutions, \( R \) the gas constant, \( T \) temperature and \( F \) Faraday constant. The superscript \( m \) refers to the membrane, respectively.

Alternatively, counter-ion transport number in the membrane phase also can be determined by the chronopotentiometry. The chronopotentiometric method is the variation of potential versus time, developed by Ramachaindraiah and Ray [160] for the variation in concentration of an electroactive species undergoing a change with time in the interfacial zone between solution and electrode has been found useful for many analytical applications including the evaluation of kinetic parameters that are directly or indirectly associated with charge.

![Fig. 13. Schematic experimental set for the determination of membrane permselectivity by membrane potential measurements.](image-url)
transfer processes [161,162]. This technique seems to be similarly applicable to the study of variation in concentration of cation/anion being transferred from the interfacial zone on one side of the ion-exchange membrane to the other. The resultant potential time data, thus obtained give more important information regarding polarization phenomena, electrical conductance, ion specificity, surface fouling, heterogeneity, and value of permselectivity and transport number of ion-exchange membrane under investigation.

In a chronopotentiometric study of ion-exchange membrane, the transition time \( \tau \) at which the concentration of electrolyte at the membrane surfaces reaches zero is expressed by Eq. (8) [160,163–169].

\[
I_{\tau}^{1/2} = \frac{ZF(DI)^{1/2}C_{i}}{2(t_{w}^{i} - t_{i})}C_{i}
\]

(8)

where \( I \) is current density, \( C_{i} \) concentration of electrolyte, \( Z_{i} \) valence of counter-ion, \( F \) Faraday constant and \( D \) diffusion coefficient. Using Eq. (8), counter-ion transport number in the membrane phase or membrane permselectivity can be calculated.

The counter-ion transport number in the membrane phase estimated by membrane potential and chronopotentiometry studies were found to be different because of apparent and true transport numbers measured by these two techniques, respectively. This difference in apparent and true transport number was attributed to either water transport number across the membrane or by the degree of membrane surface heterogeneity. Water transport number across the membrane \( (t_{w}) \) can be estimated by Seatchard equation [150,170,171], which relates apparent and true transport number by Eq. (9),

\[
t_{w}^{MT} = t_{w}^{MA} + mM_{w}t_{w}
\]

(9)

where \( m \) is the molal concentration for NaCl and \( M_{w} \) is the molar mass of the water \( (M_{w}=0.018 \text{ kg/mol}) \). With the knowledge of \( t_{w}^{MA} \) and \( t_{w}^{MT} \) values, it is easy to estimate the \( t_{w} \) value.

3.5. Electrical resistance of ion-exchange membranes

The electrical resistance of ion-exchange membranes is one of the factors that determine the energy requirements of electrodialysis processes. It may be noted that true electrical resistance is measured by AC or electrochemical impedance at certain frequency. It is however, in most practical cases considerably lower than the resistance of the dilute solutions, since the ion concentration in the membrane is relatively high. The specific membrane resistance is given as \( \Omega \text{ cm} \). From the engineering point of view, the membrane area resistance in \( \Omega \text{ cm}^{-2} \) is more convenient. As reported, membrane resistance is measured with the help of the cell composed of two black graphite electrodes fixed on plexiglass plates with known active area of electrodes as well as membrane [8,149]. Both electrodes were not in direct contact with membrane. Membrane resistance \( (R_{m}) \) is estimated by subtraction of electrolyte resistance \( (R_{sol}) \) without membrane from membrane resistance equilibrated in electrolyte solutions \( (R_{cell}) \) \( [R_{m} = R_{cell} - R_{sol}] \). Alternatively, the resistance of ion-exchange membranes is determined by current versus voltage curves in a cell, which consists of two well-stirred chambers separated by the membrane. The actual potential drop across the membrane is measured by calomel electrode. The potential drop across the membrane is determined as a function of the current density \( (I-V) \) curve. The membrane resistance is determined from the slope of the current versus the voltage drop curves, which may obtained by applying varying varied voltage across the membrane and by recording the corresponding current [171–173]. The curves consist of typical three characteristic regions. The first region is approximately the ohmic region, the second regions show the plateau, and the third region, shows a rapid increase in current. Choi et al. [174] suggested that the characteristic values of \( I-V \) curve that is \( R_{3rd}/R_{1st} \) and plateau length are closely related with the overlimiting current and electroconvection. Often different membranes with the same permselectivity may exhibit markedly different concentration polarization behavior, even though the nature of the membrane influences the concentration polarization through permselectivity only. Therefore, it is thought that the \( R_{3rd}/R_{1st} \) and plateau length values depend on the materials and the surface characteristic, such as heterogeneity, surface charge density, and distribution of the charge groups.

The effective membrane resistance determined experimentally as a function of solution concentration in equilibrium with the membrane could in principle be used for the estimation of membrane specific conductivity. The specific conductivity \( K_{m} \) of the membrane is given by Eq. (10),

\[
k_{m} = \frac{e}{A}C
\]

(10)

where \( e \) is the thickness of the wet membrane, \( A \) its area, and \( C \) its electrical conductance.

We can have further information regarding the counter-ion diffusion in the membrane phase by membrane conductance data. An ion-exchange membrane has to be considered as a micro-heterogeneous system. Among the models described in the literature, by Zabolotsky et al. [175] with consideration that membrane consists of a combination of gel phase with a relatively uniform distribution of inorganic groups and hydrophilic parts of the polymer matrix chains, on the one hand, and an electro-neutral solution filling the interstices between the elements of the gel phase, named the inter-gel phase, on the other. The inter-gel phase is the inert parts of pores, channels, and cavities. They again used the two-phase model by combining the gel phase and the inert phase into a coherent region, which can be considered as quasiheterogeneous and named the joint-gel phase or membrane phase. It was shown [176] that the micro-heterogeneous structure of the membrane material is the main factor determining the concentration dependence of membrane transport properties such as electrical conductivity, diffusion permeability, and transport numbers. Near the isoconductance point \( (K_{m}) \) the conductivity of the membrane phase, \( (K_{m}) \), and the solution phase, \( (\kappa) \), becomes equal. \( K_{m} \) was obtained from the intercept.
of the curves of conductance versus concentration \((\kappa^m - C)\). The diffusion coefficient \((D^o_i)\) of the counter-ions in the membrane phase can be calculated from the magnitude of the membrane conductivity at the isoconductance point using Eq. (10) \([175,176]\),

\[
D^o_i = \frac{RT \kappa^m_{\text{ions}}}{F^2 Q}
\]

where \(Q\) is the ion-exchange capacity of the joint gel phase.

Based on the non-equilibrium thermodynamic considerations developed by Katchalsky and Curan \([177]\), and Yamachi et al. \([178]\), membrane conductance \((\kappa)\), in combination with concentration of fixed charge in the membrane material \((X)\) data, can be used with advantage for the estimation of salt permeability coefficients \((\omega)\) in the membrane phase and frictional coefficients between solute and membrane matrix \((f\text{sm})\), for a better understanding of solute migration through the membrane. The tortuosity factor \((\theta)\), according to Shahi et al. \([34]\), and Katchalsky and Curan \([177]\), must be introduced to take into account the fact that the path of the channels within the membrane is longer than macrosopic thickness of the membrane \((l)\). \(\kappa\) is related to \(\theta\) according to Eq. (11).

\[
\theta = \frac{\kappa f^0_{1w} l}{F^2 X}
\]

\(f^0_{1w}\) is the frictional coefficient between counter-ion and water in free solution. On the other hand the solute permeability coefficient \((\omega)\) of a membrane can be described by Eq. (12) \([34,177]\),

\[
\omega = \frac{C_s \phi^2_0 \theta}{X f^0_{2w}}
\]

where \(f^0_{2w}\) is the frictional coefficient between co-ion and water in free solution. Both frictional in the free solution are defined as \([177,178]\), \(f^0 = RT/D_i\). \(D^o_i\) is the diffusion coefficient of the single ion \(i\) in the free solution.

Solutes passing through the membrane matrix face different degrees of restriction due to the interaction between the solute and membrane matrix, which may be expressed in terms of the frictional coefficient between salt and membrane matrix \((f\text{sm})\). \(f\text{sm}\) was estimated using the Eq. (13), presented by Katchalsky and Curan \([177]\).

\[
f\text{sm} = \frac{\phi^0_{\text{os}}}{\phi_{\text{os}}} \left(1 - \frac{C_s \phi^2_{\text{os}}}{X f_i}\right)
\]

Although the considerations presented here are based on certain simplifying assumptions regarding the nature of the membrane and the bathing solutions, the resulting expressions should give a clearer insight into the physical basis of some of the membrane phenomena. These membrane properties will be quite helpful during selection of ion-exchange membranes for any type of electro-membrane processes.

### 3.5.1. Electrical resistance by electrochemical impedance studies

Impedance spectroscopy has been used extensively to determine the electrical resistances of ion-exchange membranes by applying alternating current across the membrane under operating conditions \([179–182]\). Impedance measurement at a single frequency yields information about the electrochemical properties of the membrane; variation of frequency and amplitude allows differentiation between single and multilayer systems from the signal response \([183]\). Signal analysis requires modeling the structure as an interconnected system of capacitances and resistances. Membrane structure was studied using a four-terminal electrode arrangement across the membranes and porosity of the membrane could be modeled as a skin layer and support layer using the dielectric values of the polymer and the electrolyte solution used \([184]\). By varying the frequency and amplitude of the current and measuring the amplitude and phase difference of the electrical potential that develops across it, the dispersions of the conductance and capacitance can be used to distinguish between single and multilayer systems, porosity of the system, as well as the changes in the electrochemical processes. Experimental use for the impedance measurements is depicted in Fig. 14, which is a two compartment cell separated by a membrane and consists of two current electrodes and two reference electrodes.

A membrane in contact and in a state of equilibration with an electrolyte may be described by an equivalent circuit analogous to that of a Randell cell \([185,186]\). For the ideal circuit frequency dependence of impedance, \(Z\), is given by the relationship,

\[
Z = R_s + \frac{R_p - J \left(W R_s^2 C\right)}{1 + \left(W R_p C\right)^2}
\]

where, \(W = 2\pi f\), \(f\) is frequency, \(C\) is the capacitance, \(R_s\) is solution resistance, and \(R_p\) is interfacial resistance. \(Z\) can be written as follows in terms of real \((Z_R)\) and imaginary \((Z_I)\) terms.

\[
Z = Z_R + J Z_I
\]

According to Eq. (14), at low frequency limit, the imaginary term vanishes and real term approaches \((R_s + R_p)\). At the high frequency limit also imaginary term vanishes and real term approaches \(R_s\). Thus values of \(R_s\) and \(R_p\) can be estimated

![Fig. 14. Experimental cell for impedance measurements. Two Ag/AgCl electrodes are used as current electrodes (CEs), and potential across the membrane (BM) is measured with two reference electrodes (REs) using Haber–Luggin capillaries salt bridges (HLC). The solution flux (SF) is directed to the membrane to avoid concentration changes at interfacial zone.](image-url)
using limiting values of impedance at low and high frequency limit.

Impedance measurements have been used with advantages to predict the fouling of ion-exchange membranes during electro-membrane processes. The change in the value of the capacitance and resistance measured by impedance spectroscopy during fouling processes or during temperature changes can indicate where the fouling is taking place or where electrochemical or structural changes may be occurring. Fouling of electrodialysis membranes by anionic organic substances (lignosulfonate) has been followed in real time by focusing solely on the capacitance change in the electrical double layer [187]. While the overall capacitance increased, the frequency where it occurred also changed during the fouling process. While impedance spectroscopy has been used to characterize the structural and electrochemical performance of many ion-exchange membranes, biological membranes, porous membranes, and proton-exchange membranes, it is unfortunately too difficult to be carried out in many polymer membranes due to the high impedance of the material [188,189]. However, metal-coated membranes have been studied to obtain structural information. Researchers were able to demonstrate that the structures predicted by impedance measurements were consistent with those fouling with field emission electron microscopy and atomic force microscopy [190,191].

4. Applications of ion-exchange membranes

Electrodialysis using cation- and anion-exchange membranes was developed first for the desalination of brackish water and seawater. The production of potable salt still is the most important industrial application of electrodialysis. Another applications, such as the treatment of industrial effluents, the production of boiler feed water, demineralization of whey and deacidification of fruit juice, desalting of the sugarcane juice is also important. A schematic diagram detailing the important applications of ion-exchange membranes for diversified industrial requirements is presented in Fig. 15.

4.1. Electrodialysis

Electrodialysis is a mass separation process in which electrically charged membranes and an electrical potential difference are used to separate ionic species from an aqueous solution and other uncharged components. Principle of electrodialysis is illustrated in Fig. 16, which shows a schematic diagram of a typical electrodialysis cell arrangement consisting of a series of cation- and anion-exchange membranes arranged in an alternating pattern between an anode and a cathode to form individual cells. If ionic solution such as aqueous salt solution is passed through these cells under the influence of applied potential gradient between cathode and anode, the positively charged cations migrate towards the cathode and negatively charged anions towards anode. The cations pass easily through the negatively charged cation-exchange membrane but are retained by the positively charged anion-exchange membrane.

Likewise the negatively charged anions passed through the anion-exchange membrane and are retained by the cation-exchange membrane. The overall result is an increase in the ion concentration in alternate compartments, while the other compartments simultaneously become depleted. The depleted solution generally referred to as the diluate and the concentrated solution as the brine or the concentrate.

The technical feasibility of electrodialysis as a mass separation process i.e., its capability of separating certain ions from a given mixture with other molecules, is mainly determined by the properties of the membranes used in the process. The economics of the process is determined by the operating costs, which are dominated by the energy consumption and investment costs for a plant of a described capacity. Both energy consumption and investment costs are determined to a large extent by membrane properties, and operating current

Fig. 15. Schematic presentation for the diversified industrial applications of ion-exchange membrane.
density. The various process design parameters, such as flow turbulence, limiting current density, effective cell pair area, cell dimensions etc., also have the significant effect on the energy consumption and thus total operating cost.

4.1.1. Desalination of brackish water

Electrodialysis was commercially introduced during 1960s about 10 years before reverse osmosis for the water desalination. In terms of the number of installations the most important large-scale application of electrodialysis is the production of potable water from brackish water [192–198], in which electrodialysis competing directly with reverse osmosis and multistage flash evaporation. For water with relatively low salt concentration (less than 5000 ppm) electrodialysis is generally the most economical process. One significant feature of electrodialysis is that the salt can be concentrated comparatively high values (in excess of 18–20% by weight) without affecting the economics of the process severely. Most modern electrodialysis units operate with the so-called reverse polarity (EDR), i.e. anode and cathode, and with that the diluate and concentrate cell systems are exchanged periodically, preventing a scale formation due to membrane fouling. An EDR unit operates on the same general principle as a standard electrodialysis plant except that both the product and the brine channels are identical in construction. At definite interval, the polarity of the electrodes is reversed, and the flows are simultaneously switched so that the brine channel becomes the product water channel, and the product water channel becomes the brine channel. Central salt and marine chemicals Research Institute, Bhavnagar (India) installed several brackish water desalination plant of desired capacity in rural India during 1985 to 1995. Desalination by electrodialysis process had been commercialized in the United States during 1970s and several ED or EDR plants were installed. In brackish water desalination, more than 2000 plants with a total capacity of more than 1,000,000 m³ of product water per day are installed, requiring a membrane area in excess of 1.5 million m² [199]. A substantial number of installations can also be found in Russia and China for the production of potable water. Exact data, however, are difficult to obtain [199,200]. Electrodialysis desalination system powered by photovoltaic cells was also developed and installed during 1985–1995 for providing potable water from brackish water [201,202].

4.1.2. Seawater desalination

A compact apparatus for seawater desalination by electrodialysis using ion-exchange membranes was developed with a view for desalting seawater to potable water on fishing boats of 100 to 1000 tonnages. The specifications and construction of the equipment, results of polarization, practical seawater operating tests, and the costs of operating the equipment are included in Refs. [203,204]. The equipment is now available in two types, one with a production capacity of 0.5 ton/day potable water from seawater (Model SV-3) and the other with a capacity of 2 tons/day (Model SV-2). A long and continuous operation of the equipment was achieved under conditions in which the polarization limit was almost reached at the end of a one-batch desalting operation. By using wire electrodes, seawater could be used as the electrode rinse solution without acidification, which contributed to making the equipment compact and easy to operate. The cost of desalting sea water was about $1.50/1000 l by Model SV-2 and $4.00/1000 l by Model SV-3, which is fairly tolerable for use on fishing boats.

A 200 m³/day seawater desalination plant [205] by electrodialysis consisting of ten stages divided into two groups, which was modified on the basis of the plant containing twelve stages with three groups has been developed. Ruthenium-coated titanium wire electrode is used for anode and cathode, electrode compartments rinsed by high velocity and electrode polarity reversed periodically, so the plant doesn’t need any acid treatment during operation. Field trials on the first and the modified plants were carried out for 1500 and 350 h, respectively, on Meishan Island along the coast of Zhejiang Province in 1978 and 1979. Performances of both plants have been proved to be stable, but the latter is simpler and more economical than the former one.

The problem of potable water shortage in some of the islands and coastal areas of India has led to consider seawater desalination for potable purposes [206]. Electrodialysis (ED) units have been designed and fabricated to meet the demand of a section of the population of Kavaratti island (Lakshadweep, Union Territory of India). The plant having a capacity of 5.5
m³/day is based on two-stage reduction of salt wherein the first stage reduction up to 85% is achieved by recirculation of seawater. The plant commissioned in February 1989, and is running satisfactorily to its rated capacity.

4.1.3. Production of ultra-pure water

Electrodeionization (EDI) is a separation process combining ion-exchange and electrodialysis; the resulting hybrid process does not require regenerate chemicals [207–210]. This technology has been commercialized for the removal of ionic species from high-purity water but not been used in chemical processes because of unacceptable leakage rates and product loss. Electrodialysis is not an economical process for treating diluted solutions because of its high electrical resistance and loss of energy due to concentration polarization. To overcome these problems [211], ion-exchange resins were introduced into the ion-depleting compartments of an electrodialysis stack. Ion-exchange resins are polymers with fixed ionic sites that can exchange oppositely charged free ions (counter-ions). Because of their ability to exchange counter-ions, they are electrically conducted in aqueous solutions. The electrical conductivity of ion-exchange resins varies with the mobility and affinity of the counter-ions with which the resins are in contact. The ions are concentrated within the resin due to the ion-exchange capacity. Consequently, ion-exchange resins significantly reduce power consumption and increase ion transport through the membranes. Ion-exchange resins are also continuously regenerated electrochemically by hydrogen and hydroxyl ions, which are produced by water dissociation reaction in an applied electric field (DC) [212–217]. Principle of EDI using ion-exchange membranes is presented in Fig. 17. Anthony Bennett [207], a freelance writer for filtration and separation, defined high purity water, reviewed technologies available for its production and described four case studies from the USA and the UK where various process combinations have been used to generate high purity water of various grades. With a resistivity of typically 10 MΩ cm or higher and a reactive silica level (as SiO₂) of generally less than 20 µg/l, high purity water is defined along with deionized, purified, apyrogenic and ultra-pure water in Table 2.

Further processing to reduce total organic carbon (TOC) levels, together with effective storage and distribution systems, are required to process still further and produce ultra-pure water of consistently 18 MΩ cm resistivity, the highest theoretical level of purity possible. High purity water is primarily utilized in the power industry for feeding supercritical boilers and combined heat and power (CHP) systems. The removal of silica is critical to prevent deposition and mechanical failure in the steam raising systems. High purity water is also utilized in various industrial applications where cleaning of components is required. Also, these commercial EDI modules are not readily serviceable. If these limitations can be overcome, EDI will be a promising technology for product purification and water recycling because it reduces or eliminates chemical usage and waste disposal and can greatly reduce energy consumption.

4.2. Wastewater treatment

One of the most important applications of electrodialysis is in processing rinse/waste waters from the electroplating, metal finishing and metallurgical industries. In this case, complete recycle of the water and recovery of metal ions can be achieved. By the application of electrodialysis with conducting spacers, it is possible to separate/recover valuable toxic metallic ion from the wastewater up to 20 ppm level, and treated water may be utilized for cooling or wash bath [218–221]. Compare to other membrane based separation processes, electrodialysis has the advantage of being able to utilize more thermally and chemically stable membranes, so that the processes can be run at elevated temperatures and in solution of very low or high pH values. Furthermore, the concentration, which can be achieved in the brine, can be significantly higher. The disadvantage of electrodialysis is that only ionic components can be removed and additives usually present in a galvanic bath cannot be removed.

Electrodialysis has been extensively used in the electroplating industry to remove and recycle metal ions such as nickel,

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Table 2: Characteristics of deionized water, purified water, apyrogenic water, high purity water and ultra-pure water

<table>
<thead>
<tr>
<th>Type of water</th>
<th>Resistivity (MΩ cm) at 25 °C</th>
<th>Maximum microorganisms (cfu/ml)*</th>
<th>Maximum total dissolved solid, TDS (mg/l)</th>
<th>Reactive silica as SiO₂ (µg/l)</th>
<th>Total organic carbon (TOC) (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>0.05</td>
<td>Not specified</td>
<td>10</td>
<td>500</td>
<td>Not specified</td>
</tr>
<tr>
<td>Purified water</td>
<td>0.2</td>
<td>1</td>
<td>1</td>
<td>100</td>
<td>Not specified</td>
</tr>
<tr>
<td>Apyrogenic water</td>
<td>0.2</td>
<td>1</td>
<td>1</td>
<td>100</td>
<td>Not specified</td>
</tr>
<tr>
<td>High purity water</td>
<td>10</td>
<td>1</td>
<td>0.5</td>
<td>20</td>
<td>Not specified</td>
</tr>
<tr>
<td>Ultra-pure water</td>
<td>10</td>
<td>1</td>
<td>0.005</td>
<td>2</td>
<td>0.05</td>
</tr>
</tbody>
</table>

* cfu= carbon forming units.
zinc and tin from plating bath rinse solutions and also to remove inert electrolyte salts that build-up during plating [222]. Cadmium and cyanide [223] removal lead up to cadmium compound precipitation on the cation-exchange membrane limiting the use of this technique. Electro dialysis of nickel and cobalt [224] sulfate has been achieved using sulfonated polyvinyl dine fluoride (SPVDF) or Nafion 117 membranes. The major conclusion from the work is that the performance of the new SPVDF membrane was comparable to the commercial available Nafion 117 membrane for both, the electrodialysis of nickel and cobalt. Electro dialysis of mixed Ni\(^{2+}\) and Co\(^{2+}\) solutions showed the feasibility of separating nickel from cobalt by employing an appropriate complexing agent (EDTA) and membranes. An electro-permutation process [225] was employed in order to extract cations (Pb\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\) and Cd\(^{2+}\)) from diluted solutions and to produce a concentration for electrodeposition. The electro-permutation process is a modified electrodialysis procedure in which ion-exchange resins were clamped between two cation-exchange membranes. The principle of the ion transfer in an electro-permutation cell has largely been described in the literature [226–228]. Lead removal [229] from wastewater is an important problem in battery industries. The separation process by means of electrodialysis (ED) shows several advantages such as highly selective separation, high water recovery, only a partial addition of chemicals and the possibility of a stop-and-go operation. Using membranes with higher ion-exchange capacity resulted in better cell performance. Chromium recovery (Cr(III) and Cr(VI)) [230] in the using ion-exchange membranes has also been tested using ion-exchange membrane separation processes also reported.

Nitrate contamination is increasingly due to widespread use of fertilizers containing nitrate and from poorly or untreated human and animal wastes. Nitrate is also a byproduct of many industrial processes, including paper and munitions manufacturing. Deliberately effects of nitrate, especially on infants are well known. Infants are more susceptible to nitrate toxicity than older children or adults and nitrate is a serious public health threat especially to infants under 6 months of age. A long consumption of high levels of nitrate can also affect health of adults and older children, causing methaemoglobinaemia or cancer risks due to nitrosamines or nitrosamides. Hence nitrate consumption should be limited and standards have been established. A pre-selection of several commercial membranes was carried out to determine the best anionic-exchange membrane for nitrate removal. The selected membrane [231,232] transports anions in the following order: NO\(_3^-\) > CF\(^{3-}\) > HCO\(_3^-\) > SO\(_4^{2-}\). The results show that a desired product water quality can easily be obtained by electrodialysis. The electrodialysis is a simple process to remove nitrate from ground water.

4.3. Food and biotechnology

The applications of electrodialysis [233] for the food and biotechnology industries were developed for the demineralization of cane sugar juice [234], desalination of cheese whey used in ice cream, bread, cakes, sauces and infant formulas [235–237], deacidification of fruit juices [238] and to stabilize wines [239,240]. These applications use the sole property of dilution-concentration of monopolar ion-exchange membranes stacked in an electrodialysis cell. Recently, ED was used to extract cytoplasmic proteins from alfalfa [241,242] to coagulate whey proteins [243], and to reduce disulfide bonds in whey proteins [244]; these applications are based on the specific properties of electrolysis (redox reactions at the electrodes) coupled with membrane action. Apart from the monopolar membranes, use of the bipolar membranes in electrodialysis stack are increasing in the food industries for example [233], inhibition of enzymatic browning in cloudy apple juice and production of soy protein isolates.

In the conventional production processes of vitamin C there are two steps, which relate to the conversion of salts to their corresponding acids. During acidification of sodium 2-keto-\(L\)-gulonate, an ion-exchange method is commonly used. Large ion-exchange columns are employed and batch operation was used for the regeneration of ion-exchange resins. In the conversion of sodium ascorbate to vitamin C, sulfuric acid is added to the methanol solution of sodium \(L\)-ascorbate to form vitamin C, which is soluble in methanol, and sodium sulfate, which can be removed from the reaction system according to its low solubility in methanol. Vitamin C is obtained after the evaporation of methanol. Bipolar membrane electrodialysis [245–248] can be used to replace the two above-mentioned acidification processes. In this method, the ion-exchange column for the acidification of sodium gulonate and the resin regeneration can be omitted. So the process can be simplified and the acid consumed for regeneration of resins can also be saved. For acidification of sodium ascorbate, when bipolar membrane electrodialysis is employed, the conversion process can be conducted in aqueous solution, which can avoid the use of methanol and sulfuric acid.

By electrodialysis with bipolar membranes, sodium \(L\)-ascorbate and sodium 2-keto-\(L\)-gulonate can be successfully used for the production of vitamin C with 98% conversion ratio and the average current efficiency was about 70%. The electricity consumption for the electrodialytic conversion of 1 kg of vitamin C or gulonic acid is about 1 kWh [245].

Glutamine (Gln) is the \(y\)-carboxylic amidate of glutamic acid (Glu), which plays a central role in vital movements. Recent medical findings have showed that deficiency of glutamine may lead to many diseases; hence, glutamine has become a very promising new drug [249–251]. Microorganism zymo-technics is a major producing method of foodstuff-leveled Gln and medicament-leveled Gln. For the extraction of Gln from fermentation broth, the simple-root anion-exchange column separation technology was suggested [252]. However, a great amount of inorganic salts existing in the fermentation broth greatly affects the Gln separation. Hence, before the fermentation broth is separated through the anion-exchange column, it is necessary to remove the inorganic salts from it as much as possible, in which electrodialysis technology with monopolar and bipolar membranes finds wider applications [253,254].
The melassigenic ions such as alkali metal cations were suspected of being highly melassigenic by holding sugar in the molasses and preventing it from being recovered as crystalline sugar. In sugar plant much work has been carried out on the demineralization by electrodialysis of molasses, syrups and juices [255,256].

Organic acids for example, lactic, succinic, gluconic or citric acid, are increasingly used in the food, detergent or biodegradable plastics industries [257]. Their production at the industrial scale is mainly achieved by mean of fermentation from molasses, starch hydrolysates or sugars. Several unit operations are then required to get the acid having the properties in accordance with its future use. Traditional processes are designed around one or several precipitation stages, which produce large amounts of effluents with a high salt content [258]. For example, 1 kg of citric acid produced by precipitation results in the production of 2 kg of gypsum; which constitute an effluent difficult to recycle or to treat. In order to reduce this environmental impact, alternative production route using membrane operations, like electrodialysis for instance, appear very attractive and successful since the generation of effluents or by products can be significantly reduced schemes have recently been investigated [259].

Galier and Balmann [260] described the use of the ion-exchange membranes in the electrophoretic membrane reactor. This electromembrane operation offers the possibility to increase the productivity without damaging the separation efficiency compare to the electrophoresis [260–262]. The most common is electrodialysis, ED, in which ion-exchange membranes are used. However, because of the properties of the membranes, the migration of molecules of molecular weight exceeding about 500 Dalton is forbidden. The use of porous membranes in replacement of ion-exchange was then once investigated so as to extend the field of application of electrodialysis to biological molecules like polyamino acids, peptides or proteins. In that case, the porous membrane acts as a contactor and the separator. The schematic presentation [260] of the electrophoretic membrane reactor is shown in Fig. 18.

It has been clearly pointed out [260] that there is strong transfer limitations due to electrostatic interactions between the membrane and the solute. Therefore the applications of such contactors to fractionate charged solutes like polyamino acids for instance by modification of the pH, of the ionic strength or of the membrane material is still necessary. The process performances have been studied considering the purification of α-lactalbumin from its mixture with bovine hemoglobin in the solution phase. The performances of the process presented in this study are only indicative values and further work will be devoted to the improvement of the separation productivity and efficiency.

Glyoxal (CHOCHO) is a highly reactive dialdehyde [263]. Reaction of glyoxal with cellulose, starch, carbohydrates and hydrocolloids is used in paper manufacture [264], modification of adhesives containing starch, carbohydrates, and other reactive materials. In photography, glyoxal is useful in hardening gelatin, either alone or condensed with diols or amino alcohols. It is used to make a reconstituted tobacco sheet with aroma, taste, and burning characteristics of natural, whole-leaf tobacco. Glyoxal and many of its derivatives have biological activity and hence are useful in medicine, bacteriology and pest control.

Glyoxal is useful in leather tanning. Protein treated with glyoxal is more resistant to pepsin than protein treated with formaldehyde. Glyoxal is significantly less toxic than formaldehyde. Glyoxal is produced by the oxidation of acetaldehyde with nitric acid [264]. Thus, after the reaction, the product contains unreacted nitric acid, acetic acid, glycolic acid, etc., which are to be separated from glyoxal. By electrodialysis, glyoxal has been separate from nitric and organic acids with the current efficiency 75.7% and energy consumption of about 148 kWh/m³.

4.3.1. Recovery/separation of lactic acid from fermentation broth

Lactic acid has been produced commercially by fermentation since 1883 [265]. The major application of lactic acid is in the food industry as an additive and preservative. Other applications include use of a pharmaceutical intermediate, lactate ester, which is an alternative solvent to glycol ether. Lactic acid-derived polymers are becoming increasingly important because of their application within drug delivery systems and their biodegradable and thermoplastic nature means that they can be produced as high volume biodegradable plastics for packaging and other applications. However, this potential can only be realized if the cost of production is
competitive on a global scale [267–269]. Lactic acid is produced microbially from a variety of feedstock by fermentation using lactic acid bacteria (Lactobacilli). In the conversion of glucose to lactic acid by homofermentative Lactobacilli, two molecules of lactic acid are produced for every molecule of glucose consumed. pH control of this organic acid fermentation is crucial; in the absence of such pH control, the final lactic acid concentration may be less than half of that obtained with pH control [269]. Conventionally, calcium carbonate has been used to neutralize the pH during lactic acid fermentation, producing calcium lactate. Ammonium hydroxide and sodium hydroxide have also been used for neutralization, however the cost of sodium hydroxide for the neutralization of the process is dominant in the operational cost in the fermentation step [270]. As a result of pH neutralization, the product is an organic acid salt. After fermentation, the process of separating the product from the medium and converting the salt to an organic acid is complicated, involving precipitation and acidification using a mineral acid (sulfuric acid). These steps contain the major economic hurdles for organic acid production. Moreover, the processing produces large quantities of an effluent containing high concentrations of salts. For instance, in the case of calcium carbonate neutralization, 1 ton of gypsum by-product will be produced for every ton of lactic acid produced [266]. A low cost, environmentally sustainable process for organic acid downstream processing is desirable. Many investigations have been carried out into the separation, concentration and purification of organic acids from fermentation broth [265,266]. Among these, conventional electrodialysis has been developed for the separation, purification and concentration of organic acid salts from a fermentation broth, leading to economic product formation and low environmental impact of the downstream processing.

Grass silage has been considered a good candidate for the production of fine chemicals. Within “The Austrian Programme for the Development of Green Biorefinery” it was shown that during the ensiling process, lactic acid and amino acids produced make the resultant silage a potential source for the production of these substances [271]. This process is interesting due to the prospect of using cheap raw material as grass, which is a renewable resource. Amino acids are widely used as free chemicals, pharmaceutical, food or feed supplements whereby the demand for amino acids has become more significant over the years. At least 18 amino acids were found in our grass silage and an improved valorization of these amino acids requires the suitable fractionation before further purification steps. Lactic acid is used widely in numerous fields of application as food, pharmaceutical and in other industrial applications [272]. The production of lactic acid has recently attracted a great deal of interest due to its potential use as a raw material in the production of the biodegradable polylactic acid [273]. Regarding the sustainable production, it seems that lactic acid and amino acid production from grass singe is one of the promising processes. Generally, in most processes, and particularly, in the production of substances from cheap raw materials, downstream process plays a very important role and takes a big part of cost in comparison with whole production cost. The high content of salts as well as sugars makes the separation steps of grass silage juice much more difficult than that of the fermentation broth of lactic acid or amino acids, in which the sugar residue and salt content is quite low. Usual techniques, which are used for desalination, are ion-exchange, electrodialysis and partial nanofiltration. Since the salt contents are very high, ion-exchange and nanofiltration will not be economical. Thus electrodialysis can only be seen as a pretreatment step for desalination.

There are many studies about lactic acid separation from the fermentation broths by means of electrodialysis [274–280] but the final product is lactate. Danner et al. studied lactic acid purification from grass silage by electrodialysis with a high level of mineral saks in the lactate fraction [281]. Using bipolar membrane the recovery of lactic acid from lactate can be performed, where a cation- and an anion-exchange membrane sheet are laminated together [282,283]. Lactate ions associating with hydrogen ions in the feed compartment form lactic acid, and at the same time sodium ions passing through the cation-exchange membrane form sodium hydroxide with the hydroxyl ions in the permeate compartment.

The two-stage electrodialytic separation of valuable substances such as lactic acid and amino acids from grass silage juice was investigated [284]. Based on the different ionic forms of lactic acid as well as amino acids, which depend on the pH of grass juice, electrodialysis could separate lactic acid and amino acids from mineral ions. At pH = 6.7, most of the amino acids were separated from lactic acid and mineral ions. Current efficiency of the step was \( \eta = 0.67 \). The average mass transfer of inorganic salts was 0.091 kg/m²·h. The specific energy consumption for the transportation of ions through the membranes was 0.074 kWh/l of silage juice. The specific energy consumption was 2.11 kWh/kg of lactate transported. More than 97% of sugars and about 90% of amino acids were separated from the juice in the first separation step. In the further step lactic acid was separated from the previous concentrate at pH = 2. As expected, the average mass transfer of inorganic salts was 0.490 kg/m²·h, which was significantly higher than that of the first step. Current efficiency of the second step was \( \eta = 0.88 \). The specific energy consumption for the transportation of ions through the membranes was 0.038 kWh/l of silage juice. The total lactate recovered by two-stage ED was 91% at a 98% of demineralization level.

4.4. Other electro-membrane separation processes

Today, electrodialysis is by far the most important industrial membrane separation process using ion-exchange membranes. However, several other processes such as diffusion dialysis, Donnan dialysis, chlorine-alkaline electrolysis, acid–base production with bipolar membrane from corresponding salt are being used by different industries.

4.4.1. Diffusion dialysis

Various separation processes have been developed based on membranes. Diffusion dialysis is one of the oldest membrane
processes that have been established for many years where ion-exchange membranes are used instead of uncharged membranes. The membranes are arranged in parallel in a cell system, which is used in electrodialysis. There are also two flow systems. Cell pair arrangements used for the diffusion dialysis is presented in Fig. 19. One containing the feed solution and the other is so-called dialysate, which often consists of pure water. In this application, solutes pass through ion-exchange membrane when driven by a concentration difference. The process is used on a large scale to recover mineral acids from salt solution obtained in picking and etching processes [285–292]. In this application only anion-exchange membranes are installed in the stack. By feeding in the alternating cells the salt and acid mixture and a dialysate solution in counter-current flow, the individual ions will migrate from the feed solution to dialysate following the concentration gradient driving force.

While anion can easily pass the anion-exchange membranes, all cations will be more or less completely rejected, except for protons, which also are capable of passing anion-exchange membranes, due to a different transport mechanism. Therefore acids can be separated from salt mixture by diffusion dialysis using anion-exchange membranes only. When operated in counter-current flow, more than 95% of the acids can be removed from the feed solution.

Recently, heteropolysiloxane (HPS) materials containing the 2,3,11,12-bis[4-(10-aminodecylcarbonyl)]-benzo-18-crown-6 and 2,3,11,12-bis[4-(2-aminoethylcarbonyl)]-benzo-18-crown-6 compounds chemically linked in a reticulate silica matrix were synthesized by the sol–gel process [293], and were used for the preparation of dialysis membranes. These membranes were used for the facilitated competitive transport of silver/copper ions. The selectivity of the membranes is improved by the incorporation of the complexing molecules, which allow a better solubility of silver ions in the membrane.

4.4.2. Donnan dialysis

Donnan dialysis is used to exchange ions between two solutions [294–300]. The stack arrangement is identical to that used in diffusion dialysis. The principle of the process is illustrated in Fig. 20, which shows a CuSO₄ solution and 1 N H₂SO₄ separated by a cation-exchange membrane.

Since the H⁺ concentration in the acid solution (I) is significantly higher (pH = 1) than the H⁺-ion concentration in copper sulfate solution (II) (pH = 7) there will be a driving force for the transport of H⁺-ions from the solution (I) into the solution (II). Since the membrane is permeable to cations only, there will be build up of an electrical potential, which will counter balance the concentration difference driving force of the H⁺. This electrical potential difference will cause a flux of Cu²⁺ against their concentration gradient from solution (II) into solution (I). As long as the H⁺ concentration difference between the two phases separated by the cation-exchange membrane is maintained, there will be the transport of Cu²⁺ until their concentration difference is of the same order of magnitude as the H⁺ concentration difference. The process can be carried out accordingly with anions through anion-exchange membranes [299,300]. An example of the anion Donnan dialysis is the sweetening of citrus juice. In this process hydroxide ions furnished by a caustic solution replaces the citrate ions in the juice. Another application of the Donnan dialysis is softening of the hard water where divalent ions, such as Ca²⁺ and Mg²⁺, get exchanged for mono-valent ions such as Na⁺ or Cl⁻. Donnan dialysis is competing directly with conventional ion-exchange technology. In some cases, however, it is providing significant advantages in terms of reduced waste salt and ease of operation.
4.4.3. Acid–base production with bipolar membrane

In electrodialytic cell with bipolar membrane the dissociation rate of water under the influence of a direct current is \(10^6\) to \(10^7\) times faster than free solution [301,302]. This phenomenon, termed accelerated water splitting, is well known in industry where BPMs are designed for electro-synthesis of acids and bases. Separation of \(H^+\) and \(OH^-\) is accomplished without chemical addition or gas evolution, a process whose energy requirement is theoretically \(≈40\%\) of that of water electrolysis with gas evolution [303].

The principle of the electrodialytic acids and bases production with bipolar membranes from the corresponding salts is illustrated in Fig. 21. The schematic drawing shows bipolar, cation- and anion-exchange membranes arranged in parallel between two electrodes to form individual compartments. If salt is introduced in the salt stream and an electrical potential difference between the electrodes is established, the cations in the salt will migrate towards the cathode, while anions will migrate towards anode. On the other hand, water splitting will occur at the interfacial layer of the bipolar membrane resulting the formation of hydrogen and hydroxyl ions, which will move in the opposite direction and is responsible for the formation of acids and bases in the respective compartments.

One of the main interesting phenomena of electrodialysis with bipolar membrane (EDBPM) is the water splitting [304,305]. Water, which is consumed by the dissociation into protons and hydroxide ions, has to be replenished by diffusion of water from the outer solution of the two-monopolar layers into the BPM inter phase. When the rate of the water dissociation is faster than the water transport into the BPM transition region, water transport is the limiting step and results in drying out of the BPM, which causes a drastic increase in the resistance [306,307]. This performance is controlled by the permselectivities of the ion-exchange layers of the BPM and by ion diffusive transport. An additional loss of process permselectivity is obtained by the leakage through the monopolar ion-exchange membranes. Due to these leakages, the current efficiency of the process is reduced and the purity of the products is limited [305]. Another major limitation is the concentration range in which the EDBPM processes can be used. At very low concentrations, the electric resistance of the electrolyte solution in the compartments between the membranes is very high, whereas at high concentrations the selectivity of the BPM and the ion-exchange membranes is very low [308]. Additionally, the chemical stability of the BPM, especially against a concentrated base on the anion permeable side, is not always sufficient [309].

EDBPM processes can be performed with different stack configurations, depending on the desired application [304,310–312]. For the treatment of concentrated salt solutions and the production of the corresponding acids and bases, a three-compartment cell system consisting of an AEM, a CEM and a BPM as repeat unit is used (Fig. 21). In an industrial-type unit, up to 100 cell triplets could be installed in an electrodialysis stack [313]. In applications where it is not possible to obtain high purity of both products (acid and base) or products with low conductivity are produced, a two-compartment cell is then recommended [304,312]. This configuration can be used together with a CEM for acidification or with an AEM for alkalization of a salt stream [304,312]. If a high ratio of acid or base with respect to the product salt content is required, a configuration with two monopolar membranes of the same type can be applied. In this configuration, the outlet of the middle loop is recycled again into the acidic or base loop next to the BPM for a more efficient exchange between protons and cations, or between hydroxyl ions and anions [304,312]. Several applications of
EDBPM have already been investigated with promising results. Typical examples are the production of acid and base [311,314], the acidification of product streams [315,316] or special separations like the separation of amino acids and proteins on the basis of their isoelectric points [312,313].

Designing EDBPM in the overlapping areas provides increasing prospects for its economic feasibility, but it also increases the complexity and the challenges that have to be met [309]. An example of a successful overlap is the conversion of sodium lactate from a fermentation step into lactic acid by EDBPM with a use of the side product, sodium hydroxide, to control the fermentation reaction [317]. Further examples can be found in other reviews concerning EDBPM applications [304,312,318].

4.4.4. Chlor-alkali production

With the development of the chemically and thermally stable fluorinated ionomer, the chlor-alkali industry is now-a-days one of the largest industries producing annually more than 48 million tons of sodium hydroxide (NaOH) and more than 42 million tons of chlorine (Cl2) [318]. The raw material is sodium chloride (NaCl) and the reaction proceeds according to:

\[ 2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{Cl}_2 + \text{H}_2 \] (1)

In the conventional process there were two major challenges: (i) chlorine reacts explosively with hydrogen and (ii) chlorine dissolves in contact with NaOH to form a hypochlorite solution. It is therefore necessary to separate the products of the reaction. Membrane technology is the best solution for this process over other technologies like mercury cell and diaphragm cell [318].

In the membrane reactor cell, the anode and cathode are separated by means of a cation-exchange membrane (CEM) (Fig. 22). In this case, a saturated NaCl solution is passed through the anolyte compartment and Cl2 gas is produced at the anode (IrO2 usually coated with Ti). Na+ migrates through the CEM into the catholyte compartment where they combine with OH− produced in the cathode (usually Ni coated with a catalytic coating) to form hydroxide. All the electrolysis plants and designs share the following characteristics [319].

Saturated brine (300–305 g/l) is fed to the anolyte compartment and depleted brine (180–200 g/l) is discharged. The pH of the anolyte is generally kept in the range of 2–4 by addition of HCl. At higher pH, the Cl2 can react to form hypochloric acid or eventually chlorate following the reactions [320]:

\[ \text{Cl}_2 + \text{OH}^- \rightarrow \text{HClO} + \text{Cl}^- \] (2)
\[ \text{HClO} + \text{H}_2\text{O} - 2e^- \rightarrow \text{3H}^+ + \text{Cl}^- + \text{O}_2 \] (3)
\[ \text{HClO} + \text{ClO}^- \rightarrow \text{ClO}_3^- + 2\text{H}^+ + \text{Cl}^- \] (4)

However if the pH is kept too low, the competition of H⁺ and Na⁺ concerning carrying the charge will be high. The first CEM for this application was prepared by perfluorinated polymers containing sulfonate fixed ionic groups (Nafion® polymers). The Nafion® consists of a fluorocarbon polymer backbone to which sulphonic groups have been chemically introduced. These membranes could be used only up to maximum 15% NaOH concentration. At higher NaOH concentration, back migration of OH− from the cathode to the anode compartment occurred and therefore, significant loss in current efficiency in both NaOH and Cl2 was observed. The situation has been improved by using CEM containing carboxylic groups. For these membranes, the water content was lower than the sulfonic ones, and therefore, the back migration of OH− was lower. With these membranes, the production of NaOH concentration of about 32% became possible. However, due to the weak carboxylic groups, their conductivity was low and therefore, the overall cell voltage increased in comparison to CEM with sulfonic groups. Moreover when an acid anolyte is used, the carboxylic groups are protonated and the membrane resistance increases further. Much better results were obtained by using the composite membrane concept. The composite membranes have a thin layer of carboxylate polymer on the catholyte side of a basic membrane, which is made of sulfonate polymer. The composite construction uses the advantages of both types of materials. Due to the lower water content of the carboxylate polymer, the back migration of the OH− decreases but because the carboxylate layer is very thin, there is not significant increase of the membrane resistance. In addition, the carboxylate polymer is in contact with the NaOH solution and its protonation can only occur from the high flux of H⁺ through the sulfonated polymer [320]. The modern composite membranes can typically work for more than 5 years in a chlor-alkali plant. Several companies (e.g. Asahi Chemical and DuPont) are manufacturing membranes for the chlor-alkali industry. The membranes are prepared based on customer requirements by varying the equivalent weight and thickness of the two layers (sulfonic–carboxylic) or by modification of the surface to improve the hydrophilicity of the membrane or by the type of the reinforcement to improve the stability of the membrane [319].

4.5. Polymer electrolyte

4.5.1. Solid polymer electrolyte (SPE)

Ion-exchange membranes find versatile applications as solid polymer electrolytes for electro-organic synthesis, where it not only act as a proton conductor but also separates two stream, catholyte and anolyte. Also, the SPE process enables electro-organic synthesis at an electrode on the surface of an ion-exchange membrane without addition of supporting electrolytes [321]. This process was primarily developed by industry for electrolysis of pure water and for fuel cells (now usually called Proton Exchange Membrane fuel cells (PEFC)). The first applications of the SPE process for electro-organic syntheses were published by Ogumi et al. in Japan [322], then further by Sarrazin and Tallec [323] and others [324–327]. The electrode reactions take place at electro-catalytic layers at the interfaces between the membrane and permeable electrodes. The electrical current was applied with suitable current collectors to the
electrodes. Hydrogen ions are formed at the anode during oxidation and migrate through the cation-exchange membrane as solvated ion. The membrane works due to the fixed/immobilized cation-exchange sulfonic acid groups so that a conductive liquid in the cell is not necessary. Subsequently the H⁺ ions are reduced at the cathode to hydrogen. Many of these reactions were investigated with Nafion™ perfluorosulfonic acid cation-exchange membranes either uncoated (Zero Gap or Membrane Gap arrangement) or coated with an electrochemically deposited platinum layer [321] (attached porous electrode layer). No significant differences in current efficiency and cell voltage were observed between the two configurations at current densities up to 1 kA m⁻². Thus in the systems studied a direct coating of the membrane is not a necessary condition of the SPE process. Consequently, in principle, any permeable electrode material is applicable if it is stable at the conditions on the membrane surface.

The methoxylation of furane by direct anodic reaction without a mediator and supporting electrolyte using the SPE process has been reported [321]. High current efficiencies of the product dimethoxy-dihydrofurane were achieved, although high cell voltages up to 50 V were needed. By the addition of 30% water as co-solvent the cell voltage was decreased to 10 V at a current efficiency of about 60%. An auspicious examples [321] for the advantages of the SPE process using Nafion™ cation-exchange membranes, was alkylation reaction of N-alkyl-amides without any additive. Also, anion-exchange membranes were used successfully for reactions with carboxylate anions as reactants, e.g., for Kolbe synthesis with organic acids. Preliminary investigations were carried out with aqueous solutions of acetic acid or propionic acid. Using y-hydroxybutyrate anions as reactant (formed at the cathode from y-butyrolactone), which are simultaneously anion and oxidisable alcohol, the oxidation in aqueous solution without additive to succinic acid was possible in continuous operation for more than four months at a lead dioxide anode [321]. However, the use of anion-exchange membranes as SPE was limited due to the destruction of membranes by OH⁻.

Various alcohols were oxidized in aqueous media without supporting electrolyte using Nafion™ cation-exchange membranes as solid polymer electrolyte: 2-propanol, methanol and n-octanol (aqueous emulsion) at platinum/iridium gauze anodes and 2-propyne-1-01 (propargylalcohol) at lead dioxide anodes, based on sinter titanium or titanium expanded metal. Oxidation of alcohol using SPE is also important for the point of view of proton generation, which latter used for the production of H₂. Based on this technique, fuel cell technologies were developed and today find applications in large areas.

4.5.2. Proton-exchange membranes

Recently proton-exchange membranes gained broader attention for fuel cell, and electrochemical energy conversion device [328–335]. All types of fuel cells involve proton-exchange membrane, which is generally Nafion. But a lot of attention has been given to develop better proton-exchange with low fuel loss due to diffusion.

In recent years, intensive research efforts have been rendered to develop new membranes for DMFC applications [336–340]. The polymer electrolyte membrane in DMFC should not only conduct protons but also serves as a barrier for methanol; i.e., membranes have to fulfill the requirements both as effective proton conductors as well as methanol barriers. So far only a few types of membranes have been used as polymer electrolyte in DMFC, which include perfluorinated ionomer Nafion [341], polybenzimidazole/phosphoric acid blend membranes [342], Nafion membrane modified with inorganic phase such as silicate [343] and zirconium phosphate [344]. However, perfluorinated polymers have three major drawbacks: very high cost; loss of conductivity at high temperature (>80 °C); and high methanol permeability, which hinder their applicability [345]. In view of this, there is widespread effort being spent to develop alternative more economical non-perfluorinated polymer electrolyte membranes. Many promising polymers based on aromatic thermoplastics, such as poly(ether ether ketone) (PEEK), poly(ether sulfone) (PES), polybenzimidazole (PBI) etc., were studied, which have excellent chemical resistance, high thermo-oxidative stability, good mechanical properties and low cost [336–340]. By attachment of sulphonic acid groups to the polymers chain, these sulfoanted PEEK [336,346], PES [347], polyimides [348] and PBI [349] were applied as polymer electrolyte membrane. But no attention has been given to prepare suitable types of composite membranes using these polymers for the further improvement of the properties of the individuals.

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