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Ion exchange membranes and separation processes with chemical reactions

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Recent research trends in the development of ion exchange membranes and their use in separation processes with chemical reactions are reviewed. Emphasis in research on the ion exchange membrane is trending toward analysis of micro-structure of the membranes and to development of new functionalized ion exchange membranes in response to industrial requirements. Separation processes with chemical reactions are discussed according to the following classifications: (1) double decomposition of electrolytes; (2) production of acid and base by bipolar ion exchange membrane processes; (3) separators for electrolysis; (4) separators for batteries; (5) use as solid polyelectrolytes; (6) active transport through ion exchange membranes; (7) acceleration of chemical reactions by ion exchange membranes; (8) carrier transport in ion exchange membranes; (9) transducers for electrical signals from chemical reactions; and (10) modified electrodes.

1. Introduction

Since the use of ion exchange membranes has become more diverse, requirements for membranes with unusual properties have increased. These requirements have led to the development of various kinds of newly functionalized ion exchange membranes. Recently the ion exchange membrane has been used not only for the traditional applications, such as electrodialysis concentration or desalting of solutions, diffusion dialysis to recover acids, and electrolysis of sodium chloride solution, but also in various fields as a polymeric film having ionic groups. These uses are becoming more widely recognized.

On the other hand, if chemical reactions could be carried out in the membrane phase or in membrane modules and thus the products could be separated by the membrane, then chemical processes would be remarkably compact and efficient. The membrane reactor, in which enzymes and ultrafiltration membranes are used, is an example of the realization of this ideal. The modern electrolyzer for the chlor-alkali process is also an ion exchange membrane reactor.

In this work citations from recent literature and patents illustrate research trends in a variety of newly functionalized ion exchange membranes, separation processes with chemical reactions by means of ion exchange membranes and new uses of membranes as functional materials.

2. Ion exchange membranes

Ion exchange membranes are classified according to their function as follows: cation exchange membrane, anion exchange membrane, amphoteric ion exchange membrane, bipolar ion exchange membrane and mosaic ion exchange membrane. Various preparation methods have been reported [1] with recent preparation methods being: (1) the radiation grafting of a polymerizable monomer to a conventional polymer film and then introducing the ion exchange groups to the film [2]; and (2) the introduction of ion exchange groups to an aromatic condensation type polymer such as polyethersulphone and preparing an anisotropic membrane by casting and then phase inversion [3]. Radiation grafting easily imparts excellent electrochemical properties to membranes.

The phase inversion method produces an anisotropic membrane structure with a thin skin layer and a sponge layer. Plasma polymerization technology is being utilized to prepare the following ion exchange membranes: (a) anion exchange membrane by means of plasma polymerization of γ-aminopropylethoxydimethylsilan on porous polymer film [4]; (b) perfluorocarbon sulphonic acid membrane by plasma polymerization of perfluorobenzene and SO_2 [5]; (c) sulphonic acid group-containing thin film by plasma polymerization of ethylene and SO_2, or acetylene and SO_2 [6]; and (d) bipolar ion exchange membrane by graft polymerization of acrylic acid on one side of the porous polymer membrane and of N-(2-methacryloyloxyethyl)-N,N,N-trimethylammonium chloride on the other side after oxygen-plasma treatment of the porous membrane, [7] etc.

Reports indicate that Nafion membranes change into hydrogen ion permselective cation exchange membranes by treating the membrane surface with oxygen plasma [8]. Although plasma polymerization to prepare the membrane and plasma treatment of the membrane are now practiced on the laboratory scale,

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these will become an effective method for preparation of polyelectrolyte layer on devices like sensors. Various methods of preparing mosaic ion exchange membranes are also being actively studied [9].

Concurrent with studies on new membrane preparation methods, the micro-structure of the ion exchange membranes has been investigated intensively for the purpose of improving membrane performance [10]. Phase separation of hydrophilic groups in a hydrophobic polymer matrix, which results in the formation of cluster network of ion exchange groups, is well known and documented for perfluorocarbon sulphonic acid and carboxylic acid membranes [11]. The existence of micro-domains of 2.5 to 5.0 nm has also been observed by transmission electron micrograph after the perfluorocarbon sulphonic acid membrane was stained by Ruthenium tetraoxide [12]. This phenomenon may be inevitable, even in membranes heretofore considered homogeneous, since the phase separation between the hydrophilic and hydrophobic parts is also observed in sulphonated polystyrenes with differentiated degrees of sulphonation by far-infrared spectrum studies [13]. There is also a heterogeneous distribution of sulphonic acid groups, even in sulphonated polystyrene (by small-angle X-ray scattering measurement [14]).

The hydrocarbon ion exchange membranes are generally composed of derivatives of styrene-divinylbenzene copolymer and other inert polymers such as polyethylene, poly-vinyl chloride, and so on, in order to maintain the mechanical strength of the membrane. The derivatives of such copolymers are finely distributed in an inert polymer matrix forming the micro-domain because of their poor mutual compatibility as shown in Fig. 1 [15]. (The black part is PVC, stained by OsO_4, and the white part is the copolymer of styrene-divinylbenzene.) The size of the micro-domain of such copolymer changes delicately according to the species of inert polymer and monomers, polymerization conditions, etc. [16]. The abovementioned phase separation between the hydrophilic and hydrophobic components in all kinds of membranes results in water molecules of different structure existing in the membrane phase. Many studies to clarify water structure in the membrane phase have been made. For example, freezing water and non-freezing water has been estimated by use of differential scanning calorimetry [17] and local water structure near ion exchange groups has been studied by quantum mechanical calculation [18].

The heterogeneous structure of the ion exchange membrane can be utilized in some interesting ways. It is reported that perfluorocarbon sulphonic acid membrane is a suitable medium for colloidal CdS particles because clusters in the membrane provide a high concentration of finely dispersed CdS particles. For example, the CdS semiconductor particles induce the photodecomposition of formate to produce CO_2 and H_2 [19]. Electrodeposition of platinum into a perfluorocarbon sulphonic acid film on a glassy carbon electrode produces platinum particles with very high specific surface area which are highly dispersed into the film [20]. A microcomposite membrane has also been produced via the sol-gel reaction forming silicon tetraethoxide within the microphase morphology of a hydrated perfluorocarbon sulphonic acid membrane [21].

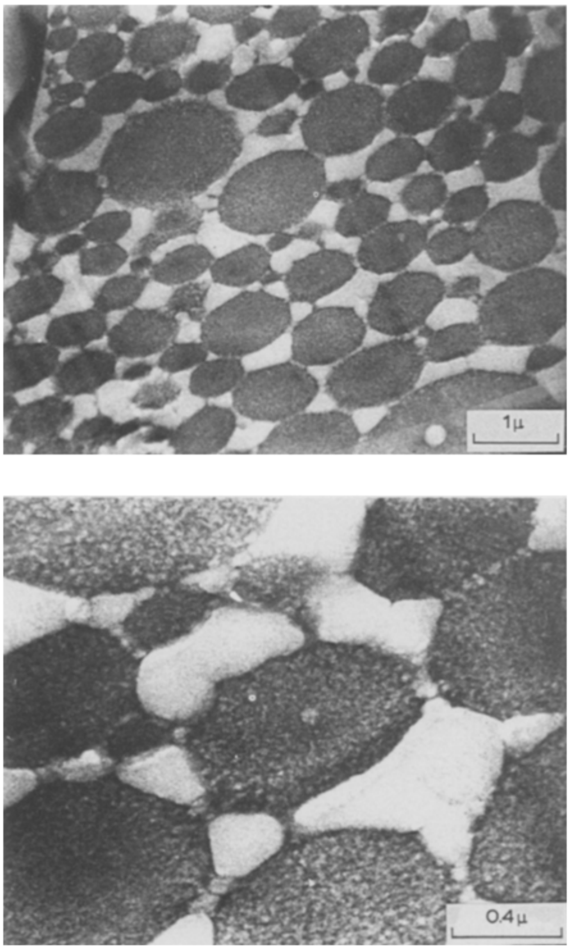

Fig. 1. Electron micrograph of cross-section of copolymer for ion exchange membrane at two magnifications. The copolymer was prepared by polymerization of divinylbenzene and chloromethylstyrene in the presence of poly-vinyl chloride.

Ion exchange membranes with specific properties, i.e., functionalized ion exchange membranes, have been developed to meet industrial requirements, such as perfluorocarbon cation exchange membranes [22] and fluorocarbon type anion exchange membrane for high temperature usage and chemical resistance [23], anion exchange membrane for diffusion dialysis to recover acids, especially nitric acid from waste acid solution [24], anion exchange membrane of high acid retention for electrodialytic concentration of dilute acid [25], hydrogen ion permselective cation exchange membrane in electrodialysis [26], monovalent cation [27] or monovalent anion permselective membrane [28], ion exchange membranes that resist [29] organic fouling, and ion exchange membranes with high mechanical strength. For example, Fig. 2 shows the change in P_{Na}^{Ca} with concentration of the solution in both conventional cation exchange membranes and monovalent cation permselective membranes, which have a cationic charged layer on the membrane

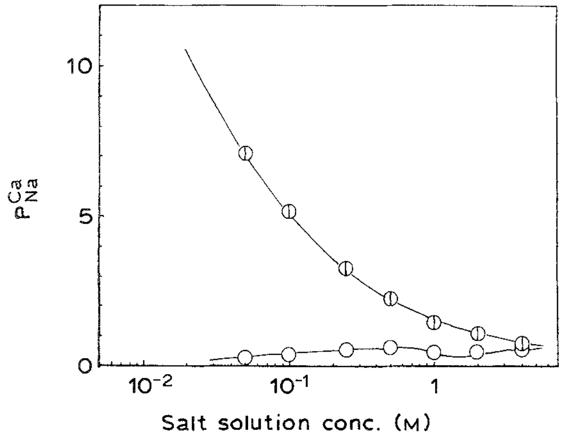

Fig. 2. Change in $P^{\mathrm{Ca}}_{\mathrm{Na}}$ with concentration of the solution. (◐) Conventional cation exchange membrane; (○) monovalent cation permselective membrane. Electrodialysis was carried out by using a 1 : 1 solution of calcium chloride and sodium chloride.

surface. ($P^{\mathrm{Ca}}_{\mathrm{Na}}$ means the equivalents of calcium ions permeating the cation exchange membrane per equivalent of permeating sodium ions.) Figures 3 and 4 show the membrane-phase ionic composition of a monovalent-cation permselective membrane and conventional cation exchange membrane both at the equilibrium state and during electrodialysis. These results suggest that the cation exchange membrane with a cationic charged layer shows monovalent cation permselectivity only during electrodialysis [30]. Nowadays, the monovalent cation permselectivity is bound permanently to the membrane surface.

Existing requirements for specific properties for ion exchange membranes include: diffusion dialysis membranes to recover acid from waste acid solution without any leakage of metal ions, and highly permselective anion exchange membranes to remove nitrate ions from drinking water [31] (although it is understandable from $P^{\mathrm{NO}_3^-}_{\mathrm{Cl}^-}$ of Table 1 that conventional anion exchange membranes in general are permselective for nitrate ions over chloride ions). Greater requirements for ion exchange membranes with other specific properties will be seen in the future, and more functionalized ion exchange membranes will be developed.

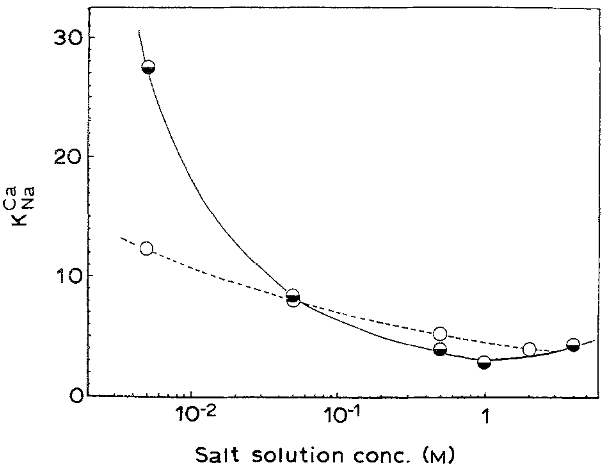

Fig. 3. Change in selectivity coefficent ($K^{\mathrm{Ca}}_{\mathrm{Na}}$), with concentration of the solution for membrane in equilibrium with the solution. (◒) conventional cation exchange membrane: (○) monovalent cation permselective membrane. A 1 : 1 solution of calcium chloride and sodium chloride was used.

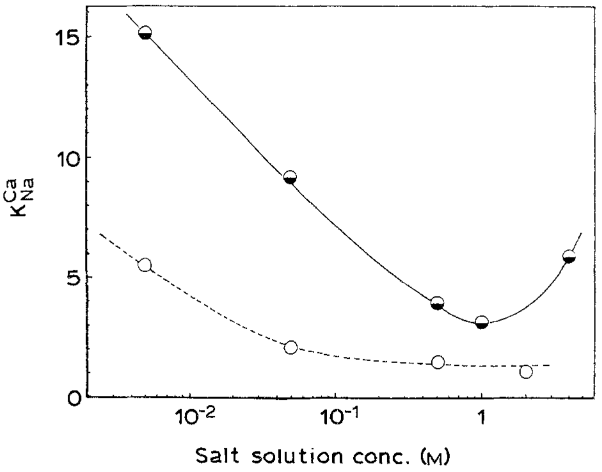

Fig. 4. Change in selectivity coefficient ($K^{\mathrm{Ca}}_{\mathrm{Na}}$), with concentration of solution in the course of electrodialysis. (◒) Conventional cation exchange membrane: (○) monovalent cation permselective membrane. A 1 : 1 solution of calcium chloride and sodium chloride was used.

3. Separation processes with chemical reactions

Studies on membrane reactors have recently increased. For example, gas phase dehydrogenation of cyclohexane to produce benzene is accelerated by removing hydrogen from the gas mixture by means of a palladium coated ceramic membrane, because the equilibrium moves to the reaction side [32]. It is also reported that conversion of acrolein from propene is accelerated by supplying electrically active oxygen to the catalyst (bismuth molybdate) on a gold anode, which is formed by chemical vapour deposition (CVD) on the oxygen permselective solid electrolyte (yttria-stabilized zirconia), with silver cathode [33]. Another reported example is improvement of the catalytic conversion of methane into ethylene and ethane over $\mathrm{LiNiO_2}$ by removing oxygen on the catalyst electrochemically by means of an oxygen pump through a stabilized zirconia electrolyte [34]. Similar examples are proposed in the case of ion exchange membranes. In a bipolar ion exchange membrane composed of a cation exchange membrane layer, a porous membrane layer containing entrapped urease and an anion exchange membrane layer, urea is

Table 1. Permselectivity of $\mathrm{NO_3^-}$ to $\mathrm{Cl^-}$ $P^{\mathrm{NO}_3^-}_{\mathrm{Cl}^-}$ in NEOSEPTA anion exchange membranes

Concn. of mixed solution	*NEOSEPTA AM-1*	*NEOSEPTA AM-2*	*NEOSEPTA AM-3*
0.25 N	4.02	4.22	4.01
0.50 N	2.34	2.67	3.06

(1) $P^{\mathrm{NO}_3^-}_{\mathrm{Cl}^-}$ means the permeated equivalent of $\mathrm{NO_3^-}$ when an equivalent of $\mathrm{Cl^-}$ permeates through the anion exchange membrane.
(2) A 1 : 1 solution of 0.125 N $\mathrm{NaNO_3}$ and 0.125 N NaCl and a 1 : 1 solution of 0.25 N $\mathrm{NaNO_3}$ and 0.25 N NaCl were used.

decomposed into NH_4^+ and CO_3^{2-} in the enzyme layer and products permeate through the respective membrane layers without application of an electric field [35]. This concept suggests the possibility of enzyme-ion exchange membrane reactors. In fermentation of ethanol, lactic acid, etc., continuous fermentation is achieved by removing products through suitable membranes [36].

Examples and possibilities of utilizing ion exchange membrane for separation processes with chemical reactions, including new application of the membrane as a functional material, are summarized in the following sections:

3.1. *Double decomposition of electrolytes*

By suitable arrangement of cation exchange membranes and anion exchange membranes, double decomposition of electrolytes, for example, $2NaCl + K_2SO_4 \rightarrow 2KCl + Na_2SO_4$, can be made by electrodialysis. In such cases the solubility of products must be sufficiently high. Although the transport number of early ion exchange membranes was relatively low, recent advanced membranes have transport numbers approaching unity and have small diffusion coefficients for electrolytes. As a result, double decomposition electrodialysis produces high purity products. Recent interesting work on fermentation production of *l*-malic acid from fumaric acid is shown in Fig. 5 [37]. Preparation and separation of pyrazine 2,3-dicarboxylic acid, which is an important intermediate in the synthesis of 2-amido-pyrazine (an antitubercular drug), from a mixed solution of potassium carbonate and potassium pyrazine 2,3-dicarboxylate [38]. This concept provides many possibilities for the synthesis of chemicals. In fact, Tokuyama Soda Co. has supplied this process to chemical, pharmaceutical and food companies.

3.2. *Production of acid and base by bipolar ion exchange membranes*

It is well known that acids and bases are produced from neutral salts by a bipolar ion exchange membrane with suitable arrangement of cation exchange membranes and anion exchange membranes. The theoretical voltage to split water into H^+ and OH^- ($H_2O \rightarrow H^+ + OH^-$) is 0.83 V, and the process is energy saving in comparison with membrane electrolysis for producing acid and base. It is known from the principles of the bipolar membrane process (Fig. 6) that current efficiencies to produce acid and base are dependent on the properties of the auxiliary cation and anion exchange membranes used in the process. Figure 7 shows that the properties of the cation exchange membrane used, together with the bipolar ion exchange membrane, have a significant effect on the current efficiency to produce caustic soda [39]. The current efficiency of acid production is also affected by the properties of the anion exchange membrane.

Many studies have been made on bipolar ion exchange membrane preparation [40]. Several catalysts to accelerate water splitting have been used in efforts to approach the theoretical voltage drop: tertiary amino groups and sulphonic acid groups [41], addition of heavy metal ions and noble metal oxides to the membrane phase [42], etc. In general, anion exchange groups (quaternized ammonium groups) are not stable in alkali solution, so a more stable anion exchange group, 1-benzyl-azonia-4-azabicyclo(2,2,2)-octane hydroxide, was examined [43].

Bipolar membranes are useful in closed-loop chemical processes, because neutral salts produced by the processes can be changed into acids and bases which are usable in the processes. Moreover, salts of organic acids and organic bases can be converted into corresponding acids and bases. Allied Signal supplies

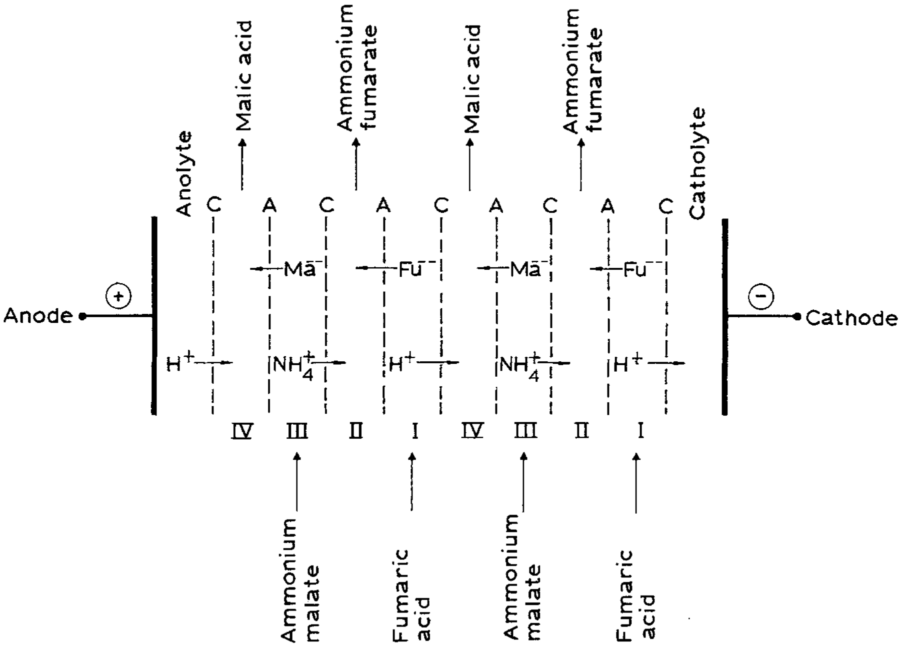

Fig. 5. Example of double decomposition of electrodialysis (production of malic acid and ammonium fumarate from ammonium malate and fumaric acid). C: cation exchange membrane; A: anion exchange membrane.

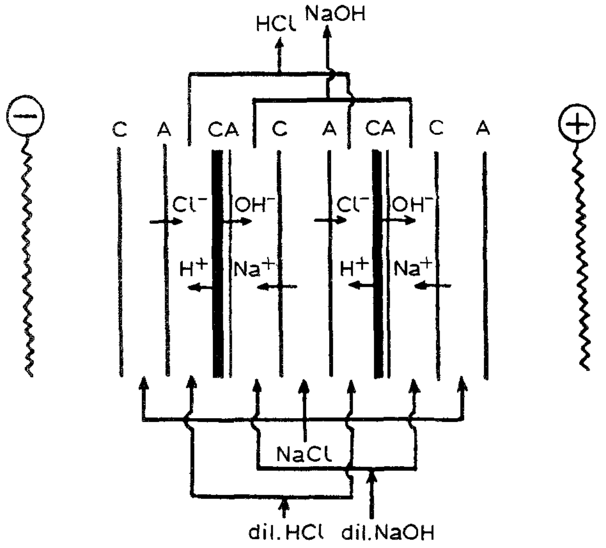

Fig. 6. Principle of producing acid and base by bipolar ion exchange membrane process. C: cation exchange membrane; A: anion exchange membrane; CA: bipolar ion exchange membrane.

the bipolar membrane process as a package. The Tokuyama Soda Company is developing the bipolar ion exchange membrane and the process together with a special cation exchange membrane and anion exchange membrane.

3.3. *Separators for electrolysis*

A typical example of a membrane reactor with an ion exchange membrane is the electrolyzer for the chlor-alkali process [44]. Since electrolysis to produce chlorine gas, hydrogen gas and caustic soda consumes substantial energy, intensive research and development efforts have been directed to the membrane process to reduce the energy consumption. Today, the energy consumption in chlor-alkali plants is only 2280 kWh tonne^{-1} of NaOH at a current density of 40 A dm^{-2} [45] and approaches the theoretical value of 1600 kWh. An effort to further reduce the energy consumption involved use of the solid polymer electrolyte (SPE – trade mark) electrolysis process, in which the opposite surfaces of a perfluorocarbon cation exchange membrane are coated by an anode catalyst and a cathode catalyst. Although SPE® electrolysis is not used industrially in the chlor-alkali process, studies have been continued in efforts to apply the process to various fields: water electrolysis to produce gaseous hydrogen and oxygen [46]; electro-oxidation of methanol in liquid phase [47] and of alcohol in vapour phase [48], etc. SPE® electrolysis has been studied for synthesis of organic reagents by oxidation or reduction such as reduction of cyclohexanol to cyclohexanone [49], reduction of various nitro- compounds [50], reduction of dibromo- compounds (for example, diethyl dibromosuccinate into diethyl fumarate [51]), oxidation of ascorbic acid to dehydroascorbic acid [52], etc. [53].

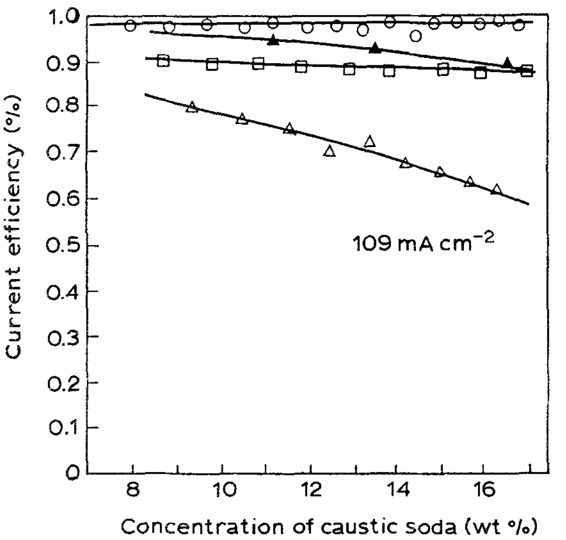

Fig. 7.. Effect of species of cation exchange membrane used in bipolar membrane process on current efficiency of caustic soda production. (○) H$^+$ generation of Aquatech bipolar membrane; NaOH production with (□) Nafion® 324, (△) Nafion® 110 and with (▲) Aquatech cation membrane.

In general, ion exchange membranes have been used as separators in electrolytic cells for organic synthesis [54]. In some cases, multiple ion exchange membranes are used as separators in electrolysis. For instance, highly pure tetramethylammonium hydroxide, an essential reagent in the development of positive photo-resist for the integrated circuit industry, is industrially produced from tetramethylammonium salt by use of an electrolyzer composed of more than three compartments [55].

Another important application of the ion exchange membrane is as a separator for electrodeposition for inaccessible parts of the surface of objects such as the inside surfaces of steel pipes, recessed parts of box-shaped structures, surfaces of metal plates located close to each other and hollow interiors. In this case, a solution of resin having carboxylate groups (ammonium salt) or resin having ammonium groups (acetate salt) is electrolyzed by using the objects as an anode or a cathode [56], and the resin is electrodeposited on the surface of the objects. The ammonium ions or acetate ions released from the resin are removed electrodialytically by use of the cation exchange membrane or the anion exchange membrane in order to maintain constant pH of the solution [57]. Today cationic electrodeposition coating is predominantly used. Recently, a tubular anion exchange membrane was developed for this purpose by Tokuyama Soda Company [58]. The most important requirement for the anion exchange membrane here is excellent mechanical strength.

3.4. *Battery separators*

A cation exchange membrane, acrylic acid grafted polyethylene film, is widely used as a separator in alkaline batteries such as the Ni–Cd secondary battery [59]. Large batteries, especially for energy storage require ion exchange membranes. Systems actively studied include: the Zn–Cl$_2$ battery, the Zn–Br$_2$ battery and redox flow batteries. For example, it is reported that a sulphonated porous polyolefin mem-

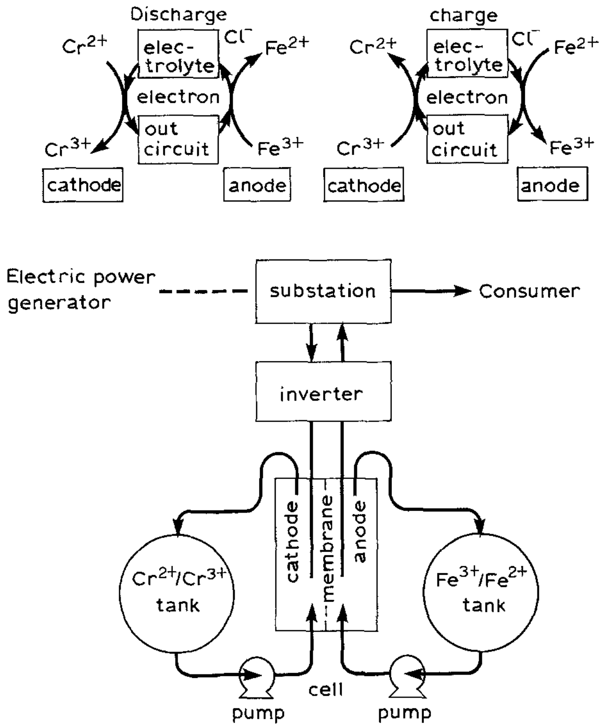

Fig. 8. Principle of Cr/Fe redox flow battery.

brane, on which styrene and divinylbenzene were grafted [60], and a membrane prepared from sulphonated polysulphone resin [61] gave good performance in the Zn–Br_2 battery. Most redox flow batteries, i.e., the chromium-iron system [62], the vanadium system [63], the ruthenium complex system with non-aqueous organic electrolyte [64], etc., require an ion exchange membrane as a separator. Figure 8 shows the principle of the Cr/Fe redox flow battery. The Cr/Fe redox flow battery has been studied actively, and both anion exchange membranes [65] and cation exchange membranes [66] are usable as the battery separator. In Japan, the Cr/Fe redox flow battery with a cation exchange membrane has been mainly studied. Requirements for the cation exchange membrane are: hydrogen ion permselectivity, low electric resistance in order to decrease impedance of the battery and low cost. These batteries have been studied for storage off-peak electric energy [67]. However, it is thought that there are still barriers to industrial application.

3.5. *Use as solid polyelectrolyte*

A typical example is of the use of an ion exchange membrane as the solid polyelectrolyte for a fuel cell [68]. The composite, in which anode catalyst, perfluorocarbon cation exchange membrane and cathode catalyst are combined, has been used for the hydrogen–oxygen fuel cell in satellites. The methanol–oxygen fuel cell is also reported to cogenerate electricity and industrial chemicals (methyl formate and CO_2) by use of a platinum-bonded solid polyelectrolyte cell [69]. Conversely, when voltage is applied to the composite in the presence of electrolyte solution, i.e., sodium chloride, organic materials, etc., electrolysis reactions occur as mentioned previously.

Currently, displays such as liquid crystal, CRT and plasma displays have an important role as interface between computers and human beings. It has been reported that a cation exchange membrane is useful as an electrolyte for electrochromic displays (ECD) [70]. In this case, the cation exchange membrane acts as proton transport media in the presence of a reversible electric field as shown in the following equation:

$$WO_3(\text{colourless}) + nH^+ \rightleftharpoons H_nWO_3(\text{blue})$$

Similarly, it is reported that polypyrrole films, prepared by electro-oxidation polymerization on a perfluorocarbon sulphonic acid polymer coated anode, show quicker response in electrochromic displays [71] and polymer complex films composed of polytetramethylene viologen and poly-p-styrene sulphonic acid (one kind of amphoteric ion exchange membrane) show electrochromic properties [72]. Although ECD is as yet used infrequently, it nevertheless has commercial application in some fields.

Another application of ion exchange membranes as proton transport media is in amperometric oxygen sensors [73] in which one side of a perfluorocarbon sulphonic acid membrane coated with catalyst contacts hydrogen gas and the other side of the membrane contacts a gas sample to determine its oxygen concentration. The oxygen partial pressure affects the current passing through the membrane.

It is reported that a composite membrane composed of polypyrrole anisotropically incorporated into an anion exchange membrane, when placed between platinum plates, produced an e.m.f. that changed with relative humidity as shown in Fig. 9 [74].

The composite membrane provides a lithium battery with an e.m.f. of 2.5 V when the membrane, swollen with propylene carbonate, is layered with lithium foil as shown in Fig. 10. Here, the anion exchange membrane layer acts as a solid polyelectrolyte for chloride

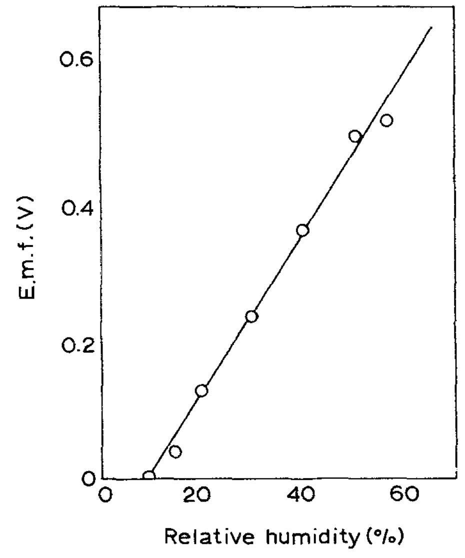

Fig. 9. Change of an e.m.f. of a composite membrane composed of an anion exchange membrane and polypyrrole with relative humidity. The composite membrane was placed between platinum plates.

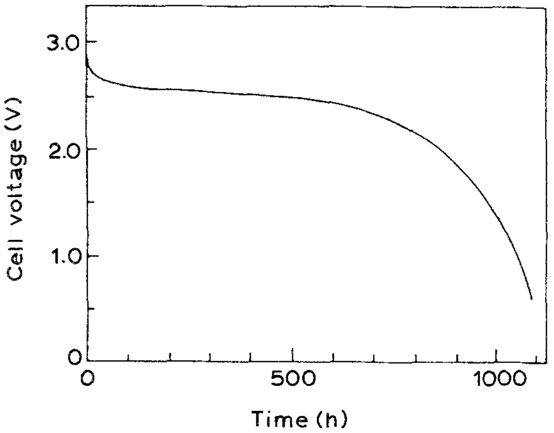

Fig. 10. Discharge curve for a Li-composite membrane battery (load resistance 2 MΩ). The composite membrane was composed of an anion exchange membrane and polypyrrole.

ions, and the chemical reactions occur on both sides of the membrane.

3.6. *Active transport through ion exchange membranes*

There have been many examples of ion transport through membranes against concentration gradients. For instance, a lactone-containing polymer membrane is permeable to sodium ions and potassium ions when the membrane is placed between a mixed solution of sodium and potassium hydroxides and an aqueous hydrochloric acid solution [75]. The same phenomena are observed when a conventional cation exchange membrane is used [76]. Similar measurements have been made for not only inorganic ions, but also amino acids [77]. For example, transport of amino acids against their concentration gradient is measured with Br^- transfer as a driving force by use of a poly(1-alkyl-4-vinylpyridinium iodide-co-acrylonitrile) membrane [78].

Another interesting phenomenon is the transport of neutral material, formaldehyde, through an anion exchange membrane [79]. As shown in Fig. 11, formaldehyde reacts with bisulphate to form hydroxymethane sulphonate, which is a conjugate base of a strong acid, and permeates through the anion exchange membrane by the coupled counter-transport of hydroxide ions. Then hydroxymethane sulphonate releases formaldehyde by reaction with hydroxide ions. The energy for transport is neutralization of hydroxide ions and hydrogen ions. Although the purpose of these studies is mainly to elucidate transport mechanisms of cell membranes, it is expected that these types of applications are of commercial importance because the energy of neutralization is high.

3.7. *Acceleration of chemical reactions by ion exchange membrane*

It is possible to accelerate chemical reactions by removing products from the reaction system before the reaction reaches the equilibrium state. Ion exchange membranes are effective in these cases. For example, the fermentation processes producing ionic materials such as acetic acid, amino acid, lactic acid, etc., can be carried out continuously by removing the products from the system through electrodialysis [80]. Figure 12 shows the principle of continuous fermentation of lactic acid by use of electrodialysis. In lactic acid fermentation by *lactobacillus delbrueckii* the produced lactic acid affected the lactic acid productivity. This inhibitory effect was alleviated by continuous removal of produced lactic acid from the fermentation broth by electrodialysis thus allowing the continuation of cell activity and high productivity

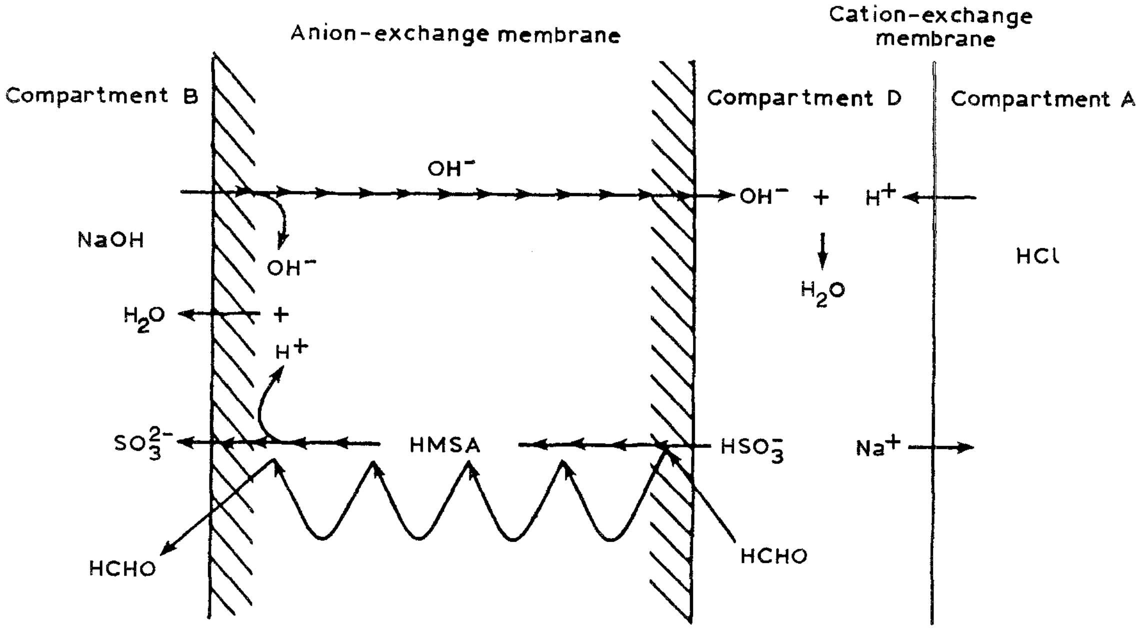

Fig. 11. Transport mechanism of formaldehyde through anion exchange membrane. [HCHO + HSO_3 = $HOCH_2SO_3^-$ (HMSA)]. HMSA: hydroxymethane sulphonate.

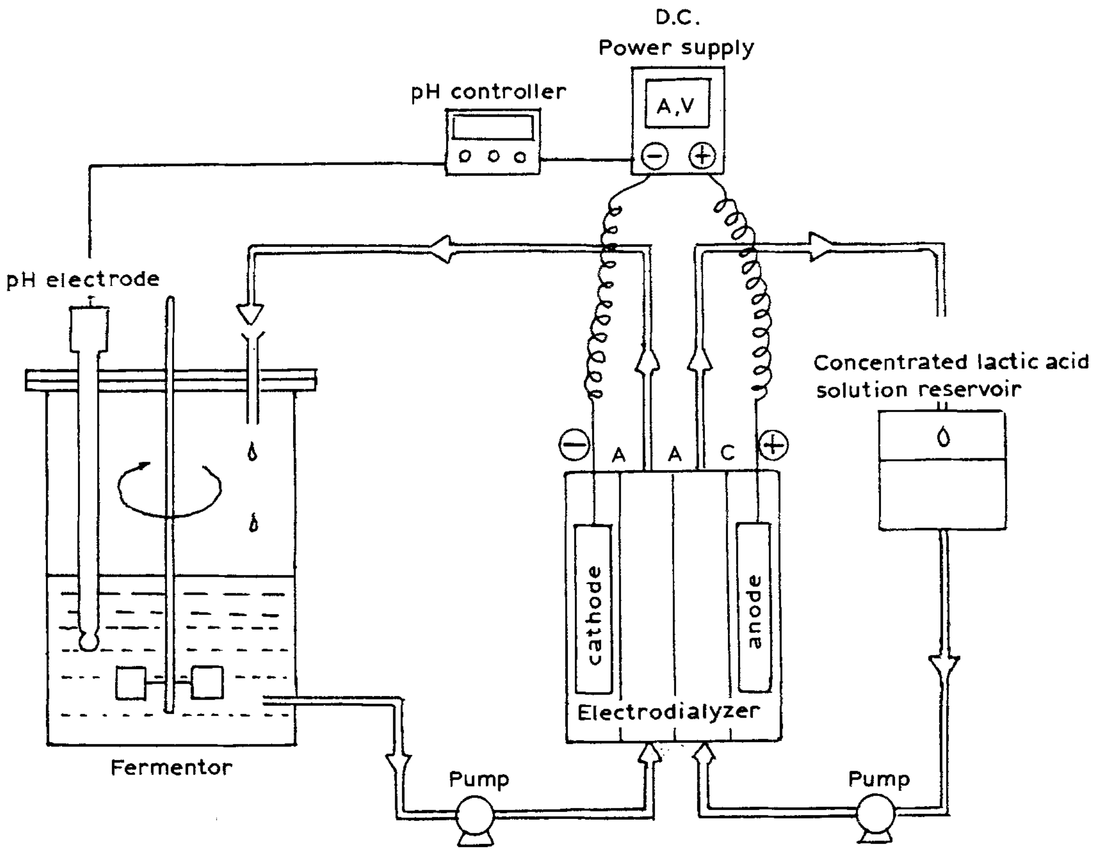

Fig. 12. Example of continuous fermentation of lactic acid by removing the product by electrodialysis.

[81]. If leakage of minerals required for fermentation through the ion exchange membrane and organic fouling of the membrane could be depressed, continuous fermentation of ionic products, i.e., amino acid, lactic acid, acetic acid, etc. may be realized in the near future.

In the case of continuous alcohol fermentation, it is desirable to remove alcohol from the fermentation broth by means of an alcohol permselective membrane. Although alcohol permselective pervaporation membranes are reported [82], the ion exchange membrane shows water permselective properties in pervaporation [83]. Therefore, the ion exchange membrane is useful for chemical reactions which are necessary to remove water. For example,

$$\text{R-OH} + \text{R}'\text{-COOH} \rightleftharpoons \text{R-OOC-R}' + \text{H}_2\text{O}$$

is accelerated by removing H_2O by pervaporation. This technique has been demonstrated for esterification of oleic acid with ethanol [84] and of propionic acid with isopropanol or propanol [85]. Figure 13 shows that pervaporation to remove water substantially increases conversion in the esterification of oleic acid with ethanol. This concept is also applicable to acceleration of chemical reactions near the equilibrium state. It is necessary for industrial realization of the process to develop high performance membranes that are durable at high temperature.

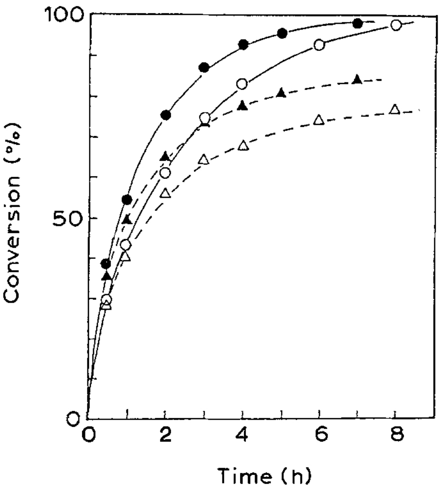

Fig. 13. Effect of pervaporation on conversion of esterification of oleic acid with ethanol. (○) mole ratio (Ethanol/Oleic acid) is 2 : 1; (●) mole ratio (Ethanol/Oleic acid) is 3 : 1. (△) and (▲) without pervaporation.

3.8. *Carrier transport in ion exchange membranes*

Transport through an ion exchange membrane is usually characterized by reversible association of the transporting species with fixed ion exchange groups in the membrane. In general, since these fixed ion exchange groups are distributed homogeneously in the membrane phase, it is possible to make another desirable carrier exist in the membrane. This type of carrier membrane is used for separation between different gases [86], different solutes, etc. For example, the cation exchange membrane ion-exchanged with ethylenediamine is effective for the separation of CO_2

from other gases. CO_2 from the gas phase is selectively absorbed on one side of the membrane to form a carbamate zwitterion, migrates through the membrane and is released from the other side of the membrane surface as shown in the following equation [87]

$$CO_2 + H_2N(CH_2)_2NH_2 \rightleftharpoons H_3N^+(CH_2)_2NHCOO^-$$

Figure 14 shows the difference of CO_2 transport between the cation exchange membrane with ethylenediamine and the membrane without the amine. Apparently, the cation exchange membrane with ethylenediamine is selectively permeable to CO_2 in comparison with the membrane without the amine [87]. It has been reported in the literature that ethylenediamine in an ion exchange membrane has been used for separating CO_2 from CH_4, H_2S, and the mixed gas of H_2S and CH_4 [88]. It has been reported recently that heat-treatment of perfluorocarbon sulphonic acid membrane in the presence of glycerol results in a high flux of acidic gas with high selectivity. This is attributed to an increase in the size of the ionic clusters of the membrane [89]. However, there is also diffusion flux of CO_2 gas through the membrane as shown in Fig. 14. It is thought that the diffusion flux exceeds the amount transported by carrier when the concentration of CO_2 gas increases to a certain level.

Incidentally, it is well known that olefins form π-complexes with silver ions. Accordingly, silver ions ion-exchanged with the cation exchange membrane naturally form a Ag^+-olefin complex in the membrane phase: $Ag^+ + \text{olefin} \rightleftharpoons Ag(\text{olefin})^+$. Carrier transport of 1-hexene and 1,5-hexadiene from the decane phase through the cation exchange membrane with silver ions has been reported [90]. Styrene permeates selectively through Ag^+- form cation exchange membranes compared with ethylbenzene [91]. Separation between 1-butene and *n*-butane was achieved with a $AgBF_4$-Nafion composite membrane [92].

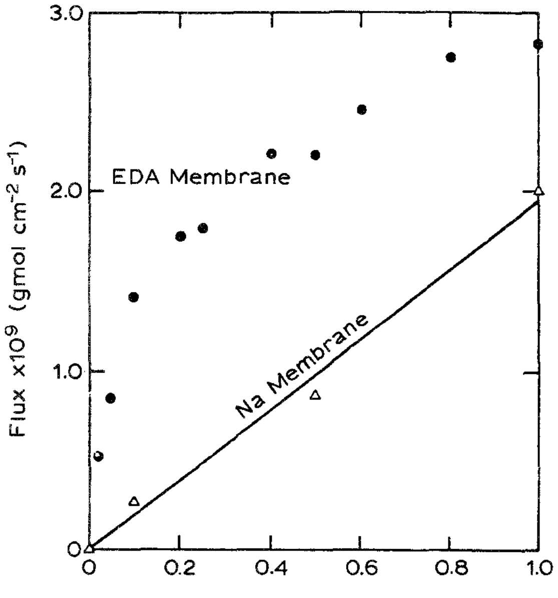

Fig. 14. Effect of feed mole fraction on CO_2 fluxes for cation exchange membrane ion-exchanged with ethylenediamine and sodium ion form membrane. (●) Facilitated flux; (△) diffusive flux.

Examples of carrier transport of ions in aqueous solution are: selective permeation of ammonia through the cation exchange membrane with Ag^+ counter ions as a carrier due to formation of an ammonia-Ag^+ complex [93] selective boric acid permeation through an anion exchange membrane with OH^- or borate counter ions as a carrier [93]. Although it is thought that there is some interaction between gases and silver metal, it is reported that perfluorocarbon cation exchange membranes in which silver metal particles distribute homogeneously are more permeable to oxygen gas than nitrogen gas. (The silver ions ion-exchanged with the membrane are reduced by high temperature hydrogen gas [94].)

As mentioned above, the ion exchange membranes are suitable materials as supports for carriers. This will become one of the interesting applications of ion exchange membranes in the future.

3.9. *Transducers for electrical signals from chemical reactions*

It is well known that the ion exchange membrane is usable as an ion sensor, because membrane potential arises by concentration difference [95]. However, as there is no specific selectivity between ions with the same charge, the utilization of the membrane as an ion sensor is limited, i.e., measurement of concentration of hydrofluoric acid. Since the specific selectivity between ions with the same charge has become controllable to some extent in recent years, the ion exchange membrane has again been studied as an ion sensor [96].

Various applications of the ion exchange membrane to other sensors have been proposed, and a few interesting examples are given here. A tough and long lasting electrode for ionic surfactants has been reported. The membrane was prepared by blending poly-vinyl chloride with cationic or anionic endgroups and high molecular weight polymeric plasticizer. This is a kind of ion exchange membrane [97]. The concentration of alcohol has been indirectly determined by consumed oxygen or generated hydrogen peroxide by use of an enzyme-membrane in which alcohol-dehydrogenase or alcohol-oxydase is fixed. However, the presence of organic acids produces erroneous results, because these are also oxidized. It has been reported that alcohol concentration can be determined accurately by use of the enzyme-fixed membrane which is coated by a cation exchange membrane, because organic acids cannot approach the enzyme-membrane [98].

The water content of ion exchange membranes changes according to humidity. As a result, the electric resistance of the membrane changes. Therefore, if electrodes are fixed on an ion exchange membrane and constant voltage is applied, the current to pass through the membrane changes according to the humidity. Studies based on this concept include:

a composite of perfluorocarbon sulphonic acid membrane and electrodes [99], a composite of sulphonated porous polyethylene sheet and electrodes [100], a hygrometer comprized of humidity permeable electrodes and surface sulphonated cross-linked polystyrene [101], and a humidity sensor with a cross-linked film of poly-4-vinylpyridine and α,ω-dichloroalkane cast on the surface of an alumina substrate with a pair of gold electrodes [102]. Photo-induced membrane potential can be used for a photosensor. Poly-vinyl chloride membrane with dipentyl phthalate and spirobenzopyran gives a membrane potential on irradiation by UV light. This is based on the reversible transformation of spirobenzopyran to a charged compound by irradiation [103].

Since a thin cation exchange membrane can be formed easily from solutions of perfluorocarbon sulphonic acid polymer (Nafion dissolved in alcohol at high temperature and pressure), this type of membrane is widely applied to various sensors: a Nafion coating on an indium–tin oxide interdigitated micro-electrode array eliminates undesired response due to ascorbic acid when catecholamines are determined by the array [104]; a regioselective electrode for nitrophenols coated by a perfluorocarbon sulphonic acid film [105]; Nafion-coated electrode for electrochemical determination of cationic medicines, i.e., acetylcholine, hexamethonium, nicotine, etc., based on the competitive partition between (ferrocenyl methyl) trimethylammonium ions and cationic medicines into the Nafion layer [106], etc. Some of these examples are already in industrial use.

3.10. *Modified electrodes*

Some modified electrodes are composites of electrodes and ion exchange membranes. Cross-linked poly-N-alkylpyridinium and perfluorocarbon sulphonic acid polymers are often used for modification of electrodes. For example, the electrode coated with cross-linked poly-N-alkylpyridinium has been studied to use redox reactions such as $[Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6]^{3-}$ [107]. There have been many similar studies.

In order to obtain quinone and hydroquinone by electrochemical oxidation of benzene with high current efficiency, an anode modified by a bipolar ion exchange membrane has been used [108]. The bipolar ion exchange membrane used was composed of a protonated poly-4-vinylpyridine layer and a perfluorocarbon sulphonic acid polymer layer. $[Fe(CN)_6]^{3-}$ was incorporated in the inner layer (poly-4-vinylpyridine) and was not contained in the solution. Release of $[Fe(CN)_6]^{3-}$ from the inner layer was prevented by the outer layer (perfluorocarbon sulphonic acid polymer layer). As a result, redox catalysts, i.e., Cr^{6+}/Cr^{3+}, $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$, etc., incorporated in the bipolar ion exchange membrane on the electrode surface accomplish the catalysis more efficiently than if they were dissolved in the electrolyte solution. The membrane on the electrode surface acts as an electron transport media. This is an interesting application of ion exchange membranes to modified electrodes. Other similar trials have been reported: RF-plasma treatment of perfluorocarbon cation exchange membrane coated on an electrode to control the permeability of redox species such as $Ru(bpy)_3Cl_2$, 1,1-dihydroxymethyl-ferrocene [109], etc. The membrane containing redox carrier has been studied, not only on the electrode surface, but also to perform redox reactions in the solution, e.g., reduction of $K_3[Fe(CN)_6]$ by $Na_2S_2O_4$ solution across a membrane composed of polypeptide with viologen moieties as functional groups [110]. Although the durability of the modified electrode and of the membrane containing redox carrier are not clear, these have great possibilities in membrane reactor application.

4. Conclusion

Synthesis of chemicals usually requires chemical reaction and separation processes. Membranes may contribute to the chemical reaction and the separation process being carried out simultaneously. This objective is achieved in the chlor-alkali membrane process. In general, the separation process is very complicated in organic synthesis, especially biosynthesis in comparison with inorganic chemistry. This is the reason why membrane reactors have been actively studied in bio-synthesis in recent years.

Ion exchange membranes are interesting material for separation processes with chemical reactions. In fact, since cation exchange groups are acidic and anion exchange groups are basic, ion exchange membranes themselves are membranous catalysts. As the ion exchange groups are relatively stable, the membrane is tolerant to high temperature, organic solvents, oxidizing agents, etc., with proper selection of a backbone polymer for the membrane. It is also easy to introduce catalyst, enzyme, carrier, etc., through the ion exchange groups. In this paper, a wide variety of separation processes with chemical reactions involving ion exchange membranes have been reviewed. It is expected that these types of application of ion exchange membranes will spread widely.

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