

PREPARATION AND CHARACTERIZATION OF ION-EXCHANGE MEMBRANES

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Summary

Preparation and characterization of ion exchange membranes are described. After the

ion-exchange membranes were classified from their functions, general methods to prepare the ion-exchange membranes are explained: such as heterogeneous ion-exchange membranes, membranes prepared from condensation of monomeric compounds and membranes prepared by polymerization of vinyl monomers such as styrene, divinylbenzene, chloromethylstyrene, perfluoro(vinyl monomer) having functional groups. Subsequently, various methods to prepare cation exchange membranes and anion exchange membranes are explained in detail. Thereafter, the ion-exchange membranes having special functions in addition to separation between cations and anions are described: cation exchange membranes having permselectivity for monovalent cations, anion exchange membranes having permselectivity for a specific anion, anion exchange membranes with high acid retention, anti-fouling ion-exchange membranes, ion-exchange membranes for diffusion dialysis, cation exchange membrane for chlor-alkali production, bipolar ion-exchange membranes and mosaic ion-exchange membranes.

Measuring methods of characteristics of the ion exchange membranes are also explained in detail: electrical resistance of the membranes, transport number of counter ions, ion exchange capacity and water content of the membranes, diffusion coefficient of electrolytes through the membranes, water transport through the membranes and chemical stability of the membranes. Finally, characteristics of some commercial ion exchange membranes are listed.

1. Introduction

The discovery of ion-exchange phenomena in minerals and the explanation of biological phenomena are the origins of studies on ion-exchange membranes. Modified collodion membranes were among the first charged artificial membranes (Abrams and Sollner 1943). After ion-exchange resins were developed, heterogeneous ion-exchange membranes, which are prepared from powdered ion-exchange resins and binding polymers, were reported (Wyllie 1954). The first paper on the preparation of ion-exchange membranes was published in 1950 (Juda and McRae 1950). Since then, the ion exchange membranes have been examined in various separation processes: electrodialysis, separators for electrolysis, diffusion dialysis, Donnan dialysis, piezodialysis, reverse osmosis, etc., because of permselectivity of ions, pervaporation to dehydrate organic solvents, dehumidification of gases, because of hydrophilicity of the membranes, gas separation such as acidic gas, because of existence of a fixed carrier, etc. In addition, the membranes have been evaluated as sensing materials such as gas sensors, humidity sensors and drug sensors. Today the ion-exchange membranes are widely used in various industrial fields: electro-dialytic desalination of saline water, concentration of salt solution such as electro-dialytic concentration of seawater to produce edible salt, removal of electrolytes from nonelectrolyte solutions by electrodialysis such as demineralization of whey, a separator for electrolysis of sodium chloride to produce chlorine gas, sodium hydroxide and hydrogen gas, recovery of acids and alkalis from waste acids and alkalis by diffusion dialysis, etc. In particular, in recent years, the concentration of nitrate ions in groundwater has been greatly increasing in parts of European countries because of excess use of artificial fertilizer. This is a serious problem because nitrate ions are harmful to human health. Electrodialysis is one of the effective methods to solve the problem because nitrate ion permselective anion

exchange membranes can be prepared (Sata et al. 1995a). On the other hand, electro-deionization (EDI), in which ion-exchange resins and ion-exchange membranes are combined, is an effective method to obtain ultrapure water continuously without any discharge (Ganzi 1988, Dejan et al, 1997). For these purposes, many methods of preparing ion-exchange membranes have been proposed. About half a century has passed since the first publication and excellent ion-exchange membranes have been developed. Today, ion-exchange membranes have become one of the essential human life support materials. Here, preparation methods which have been reported are summarized and the main preparation methods which are used today are explained.

2. Classification of Ion-exchange Membranes

There are different methods of classifying ion-exchange membranes: based on their function; materials constituting the membranes, etc. Classification based on function is clear; ion-exchange membranes have an electrical charge, which is positive or negative. The function of ion-exchange membranes is determined from the species of the charge of the ion-exchange groups fixed in the membranes and their distribution:

1. Cation exchange membranes, in which cation exchange groups (negatively charged) exist and cations selectively permeate through the membranes.
2. Anion exchange membranes, in which anion exchange groups (positively charged) exist and anions selectively permeate through the membranes.
3. Amphoteric ion exchange membranes, in which both cation and anion exchange groups exist at random throughout the membranes.
4. Bipolar ion-exchange membranes which have a cation exchange membrane layer and anion exchange membrane layer (bilayer membranes).
5. Mosaic ion exchange membranes, in which domains having cation exchange groups exist over cross-sections of the membranes and domains of anion exchange groups also exist. An insulator may exist around the respective domains.

In cation exchange membranes, the ion-exchange groups used are sulfonic acid, carboxylic acid, phosphonic acid, monosulfate ester, mono- and diphosphate ester groups, hydroxylic groups of phenol, thiol, perfluoro tertiary alcohol groups, and other groups which provide a negative fixed charge in aqueous or mixed water and organic solvent solutions. Anion exchange groups are positively charged groups: primary, secondary, and tertiary amino groups, quaternary ammonium groups, tertiary sulfonium groups, quaternary phosphonium groups, cobalticinium groups (Ito and Kenjo 1968), groups which provide a positive fixed charge in aqueous or mixed water and organic solvent solutions such as crown ethers with alkali metals (Rubinstein et al. 1984). However, sulfonic acid and carboxylic acid groups are mainly used as cation exchange groups, and quaternary ammonium groups such as benzyl trimethylammonium groups and *N*-methyl pyridinium groups are mainly used as anion exchange groups in practical ion-exchange membranes. Though there are various ion-exchange membranes based on the above listed species of ion-exchange groups and their distribution, most of the ion-exchange membranes used in industry are cation exchange membranes having sulfonic acid and/or carboxylic acid groups, and anion exchange membranes with quaternary ammonium groups.

Based on the materials of the ion-exchange membranes, such membranes can be classified as: (1) membranes composed of hydrocarbons or partially halogenated hydrocarbons; (2) perfluorocarbon membranes; (3) inorganic membranes; and (4) composite membranes of inorganic ion-exchanger and organic polymer. In recent years, natural polymers such as alginate and chitosan have been actively examined as materials of ion-exchange membranes (Uragami 1987).

3. Preparation of Ion-exchange Membranes

3.1. General Preparation Methods

Basically, three basic properties are required for ion-exchange membranes: (1) to exist as a membrane; (2) to be insoluble in solvents; and (3) to have fixed charges in the membrane. To achieve these properties, many methods have been developed: after ion-exchange groups are introduced in a polymer, the polymer is changed into an insoluble membrane; a polymeric membrane is produced and ion-exchange groups are then introduced in the membrane, etc. Various preparation methods for ion-exchange membranes which were reported in papers and patents are classified as follows.

3.1.1. Heterogeneous Membranes

After finely powdered ion-exchange resins and a thermoplastic polymer (binder of the resins), such as a polyolefin, are homogeneously blended by melting and mixing, the polymer blend is formed into a thin film with a backing fabric such as polyethylene net. Though the electrochemical properties of the membranes are slightly inferior to homogeneous ion-exchange membranes, the membranes have great mechanical strength and are easy to prepare (Wyllie 1954).

3.1.2. Membranes Prepared from Condensation of Monomeric Compounds

Sodium phenol sulfonate, phenol and formaldehyde are easy to form into a condensation polymer by heating in the presence of an alkali catalyst. After preparing a viscous polymer with low molecular weight from the monomers, prepolymers may be coated on a reinforcing fabric such as a glass fiber fabric and cured to complete the condensation reaction in the presence of drying. Similarly, phenylenediamines, phenol and formaldehyde are used for the preparation of anion exchange membranes. The membranes are immersed in salt or acid solutions (Ishibashi et al. 1954, Haagen and Helfferich 1959, Onoue et al. 1959). Though the preparation of such membranes is easy, their durability is not sufficient for long term electro dialysis.

3.1.3. Membranes Prepared by Polymerization of Vinyl Monomers

Various preparation methods using vinyl monomers have been reported, and most commercially available homogeneous ion-exchange membranes are prepared in this way.

1. After styrene is partially polymerized by heating, divinylbenzene, a peroxide such as benzoyl peroxide (an initiator of polymerization), additives such as dioctyl

phthalate, etc., and additional styrene are added to the partially polymerized polystyrene. The mixture of the linear polymer and the monomers is then polymerized into a block, and the block is cut into slices. Ion-exchange groups such as sulfonic acid groups are introduced into the sliced films (Tsunoda et al. 1958). Changing the mono-vinyl monomer to a monomer such as acrylic acid, vinyl pyridines, etc., instead of styrene provides other types of ion-exchange membranes. Though the membranes prepared by this method show low electrical resistance due to the absence of reinforcing fabric, the mechanical strength is not sufficient.

- After linear polymers such as poly(vinyl chloride), polyethylene, styrene-butadiene rubber, acrylonitrile-butadiene rubber, etc., are added to a mixture composed of plasticizer and vinyl monomers such as styrene and divinylbenzene, chloromethylstyrene and divinylbenzene, vinylpyridines and divinylbenzene, etc., to obtain a pasty mixture, the mixture is coated on a backing fabric (cloth or net) and covered with a separating film such as poly(vinyl alcohol), polyethylene terephthalate, etc., on both sides. The composite is then heated to produce a plastisol and to copolymerize the vinyl monomers. The film obtained is reacted with reagents to introduce ion-exchange groups. An alternative method of this type involves polymerizing a mixture of vinyl monomers, peroxide and additives, or a mixture of vinyl monomers, peroxide, additives and linear polymers on a reinforcing fabric between two glass plates or between plastic films which are rolled. Most commercial hydrocarbon-type ion-exchange membranes are manufactured by this method. The obtained ion-exchange membranes show excellent electrochemical properties, sufficient mechanical strength and are easy to manufacture in large volume. Figure 1 shows an example of a schematic diagram of the preparation method for a precursor membrane (Mizutani et al. 1963, 1965).

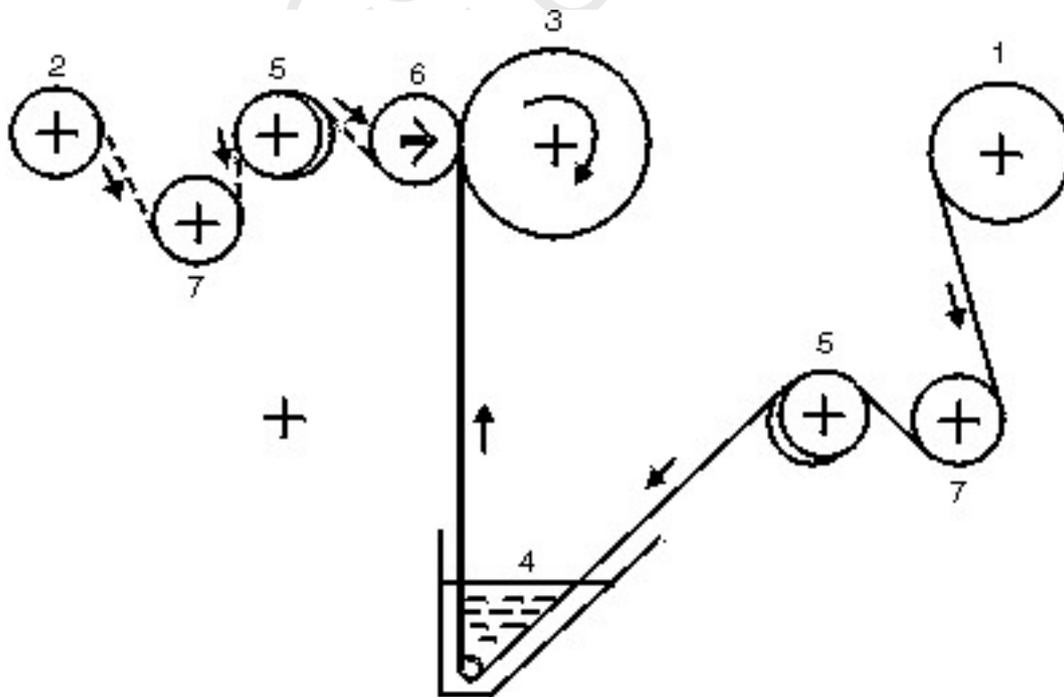


Figure 1. Example of preparation method for precursor membrane by coating. 1 -

reserve roll of reinforcing material (cloth); 2 - reserve roll of separating film; 3 - receiving roller; 4 - reservoir for paste (mixture of vinyl monomers, linear polymer, peroxide, etc.); 5 - expander rollers; 6 - pressure roller; 7 - guide rollers.

In recent years, vinyl monomers having functional groups, which are already ion-exchange groups or are easy to convert to such groups, have become commercially available. Alternative crosslinking reagents such as ethylene glycol dimethacrylate are also available. On the other hand, reagents for introduction of the ion-exchange groups into the copolymer membranes mentioned above are frequently harmful to human health and to the environment: chlorosulfonic acid, sulfuric acid, trimethylamine, etc. Therefore, it is desirable to prepare membranes from vinyl monomers already having functional groups thereby eliminating the use of such harmful reagents: anion exchange membrane prepared by copolymerization of ethylene glycol dimethacrylate and $\text{CH}_2 = \text{C}(\text{CH}_3) - \text{COOCH}_2\text{CH}_2\text{NR}_n$ (R : alkyl groups; n : 1-2) and alkylation (MacDonald 1991), cation exchange membrane prepared by copolymerization of *N*-benzyl trimethylammonium styrene sulfonate and divinylbenzene (MacDonald 1993). Many preparation methods for membranes to eliminate the use of harmful reagents have been proposed (Hodgdon et al. 1992).

Vinyl monomers swell some kinds of polymer films: styrene and divinylbenzenes swell poly(vinyl chloride) film substantially. After a polymer film such as poly(vinyl chloride), polyethylene, poly(chlorotrifluoroethylene), etc., is swollen in a vinyl monomer mixture containing a radical initiator, the film is covered with films, for example, cellulose film and heated to polymerize the monomers. Ion-exchange groups are introduced into the thus obtained precursor membrane, such as by sulfonation, chloromethylation and amination, etc. (Dimov and Alexandrova 1983). Though ion-exchange membranes are easy to prepare by this method, the transport number of counter ions in such membranes is relatively low although the electrical resistance is also low.

Radiation-induced grafting of vinyl monomers on commercially available polymer films is also an effective method of preparing ion-exchange membranes and their precursors. Polyethylene, poly(tetrafluoroethylene), etc., are irradiated e.g. by an electron beam, or γ -rays from Co^{60} , to form radicals in the polymers and vinyl monomers are grafted into the film. There are two cases: the radiation is carried out in the presence of vinyl monomers, or after the irradiation of the polymer films, the films contact the vinyl monomers (pre-irradiation). In recent years, many papers have been published on the preparation of the ion-exchange membranes by this method. The thus obtained membranes show excellent performance (Tabaddor et al. 1979, Omichi and Okamoto 1982, Hegazy et al. 1984, Uschold 1984, Chakravorty et al. 1989).

3.1.4. Preparation of Membranes from Conventional Polymers

Membranes can be prepared from commercially available polymers. Various methods have been studied because it is thought that the membranes are easy to prepare.

1. Commercially available polymer films such as polyethylene, poly(vinyl chloride), poly(vinylidene fluoride), etc., are directly reacted with reagents to introduce ion-

exchange groups e.g. with concentrated sulfuric acid; a mixture of SO₂ and Cl₂ gas to introduce sulfonyl chloride groups; chlorosulfonic acid; trimethylamine, etc. (Richard 1964, De Kórósy and Zeigerson 1967, von der Velden 1977). For example, after polyethylene film is reacted with a mixture of SO₂ and Cl₂ gas to introduce sulfonyl chloride groups, the membrane is then reacted with sodium hydroxide solution to hydrolyze the sulfonyl chloride groups to sodium sulfonate. Alternatively, the membrane is reacted with a diamine having both tertiary amino groups and primary or secondary amino groups to introduce tertiary amino groups in the membrane by acid-amide bonding. The pendant tertiary amino groups may be quaternized. Some commercial ion-exchange membranes have been prepared by this method.

After a linear polymer having ion-exchange groups is prepared from commercially available polymers such as polystyrene, polysulfone, poly(vinylpyridines), etc., a solution of the polymer or a mixture of the polymer and inert polymers is cast on a flat plate, dried and the resultant polymer film is used as the ion-exchange membrane (Gregor et al. 1957). In some cases, a crosslinking reaction is carried out, if necessary (Mizutani et al. 1962). In recent years, engineering plastics such as poly(phenylene oxide), polysulfone, poly(ether sulfone), poly(ether ether ketone)(PEEK), etc., have been actively studied for this method. Not only dense membranes, but also porous and asymmetric ion-exchange membranes can be prepared by the phase inversion method (Huang and Kim 1984).

A latex of polymers in which ion-exchange groups are easily introduced is also usable for preparing a precursor of ion-exchange membranes. For example, a viscous latex of a copolymer of styrene and butadiene is coated on a woven fabric and dried to obtain a precursor membrane. The latter is reacted with a Lewis acid to crosslink double bonds in the polymer and ion-exchange groups are introduced (Hani et al. 1960). In the case of a cation exchange membrane, because sulfuric acid is a Lewis acid, both crosslinking and sulfonation of the latex based membrane can be done at the same time by selecting a proper concentration of sulfuric acid.

3.1.5. Extrusion of Thermoplastic Polymers having Precursor Groups of Ion-exchange Groups into a Polymer Film and Conversion of the Groups into Ion-exchange Groups

Non-crosslinked perfluorocarbon-type cation exchange membranes are prepared by this method. Copolymers of tetrafluoroethylene and perfluoro(alkylvinylether sulfonyl fluoride) or perfluoro(vinylether carboxylic acid ester) such as perfluoro(3,6-dioxa-4-methyl-7-octene-sulfonyl fluoride), methyl perfluoro(5-oxa-6-heptenoate), methyl perfluoro(5,8-dioxa-6-methyl-9-decenoate), etc., are extruded in a thin film. The sulfonyl fluoride or alkyl carboxylate of the films are hydrolyzed into sulfonate groups or carboxylate groups, respectively. Usually, the ion-exchange membranes are reinforced with a woven fabric made of perfluoro polymers. Because the perfluorocarbon cation exchange membranes have excellent durability in contact with strong oxidizing reagents, new applications of such ion-exchange membranes have been developed: separators for electrolysis of sodium chloride solution (Eisenberg and Yeager 1982), solid electrolytes for hydrogen-oxygen fuel cells, solid electrolytes for water electrolysis, etc.

3.1.6. Preparation of Ion-exchange Membranes by Plasma Polymerization

Vapors of trifluoromethane sulfonate, 4-vinylpyridine, etc., are polymerized by plasma, and the formed polymers are deposited on a porous substrate. Various monomers can be used in this method. For example, a vapor of trifluorochloroethane and trifluoromethane sulfonic acid is polymerized by a radio frequency plasma (Ogumi et al. 1990a; Brumlik et al. 1994). These studies are trials to prepare perfluorocarbon cation exchange membranes by a simple method. Anion exchange membranes are also prepared by the same method using 4-vinylpyridine (Ogumi et al. 1990b). Another method using plasma polymerization involves grafting vinyl monomers such as vinyl pyridines, acrylic acid, methacrylic acid, etc., on a substrate such as an ion-exchange membrane (Ogumi et al. 1990c), porous membrane (Matsuyama et al. 1994), etc., after the formation of radicals on the substrate by sputtering with oxygen plasma or glow-discharge plasma of the inductively coupled type.

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