

Review

Ion exchange membranes: State of their development and perspective

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Abstract

During the last 50 years, ion exchange membranes have evolved from a laboratory tool to industrial products with significant technical and commercial impact. Today ion exchange membranes are receiving considerable attention and are successfully applied for desalination of sea and brackish water and for treating industrial effluents. They are efficient tools for the concentration or separation of food and pharmaceutical products containing ionic species as well as the manufacture of basic chemical products. The evolvement of an ion exchange membrane not only makes the process cleaner and more energy-efficient but also recovers useful effluents that are now going to wastes, and thus makes the development of society sustainable. Therefore, the intention of this review is to give a brief summary of the different preparation and characteristics of ion exchange membrane as well as their potential applications. The most relevant literatures in the field are surveyed and some elucidating case studies are discussed, also accounting for the results of some research programs carried out in the author's laboratory. © 2005 Elsevier B.V. All rights reserved.

Keywords: Ion exchange membranes; Amphoteric ion exchange membrane; Bipolar membrane; Mosaic ion exchange membranes; Hybrid ion exchange membrane; Electrodialysis

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1. Introduction

Traditionally, ion exchange membranes are classified into anion exchange membranes and cation exchange membranes

depending on the type of ionic groups attached to the membrane matrix. Cation exchange membranes contains negatively charged groups, such as $-\text{SO}_3^-$, $-\text{COO}^-$, $-\text{PO}_3^{2-}$, $-\text{PO}_3\text{H}^-$, $-\text{C}_6\text{H}_4\text{O}^-$, etc., fixed to the membrane backbone and allow the passage of cations but reject anions. While anion exchange membranes contains positively charged groups, such as $-\text{NH}_3^+$, $-\text{NRH}_2^+$, $-\text{NR}_2\text{H}^+$, $-\text{NR}_3^+$, $-\text{PR}_3^+$,

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$-\text{SR}_2^+$, etc., fixed to the membrane backbone and allow the passage of anions but reject cations [1,2]. According to the connection way of charge groups to the matrix or their chemical structure, ion exchange membranes can be further classified into homogenous and heterogeneous membranes, in which the charged groups are chemically bonded to or physically mixed with the membrane matrix, respectively. However, most of the practical ion exchange membranes are rather homogenous and composed of either hydrocarbon or fluorocarbon polymer films hosting the ionic groups [3].

The development of ion exchange membrane-based process began in 1890 with the work of Ostwald [4] who studied the properties of semipermeable membranes and discovered that a membrane can be impermeable for any electrolyte if it is impermeable either for its cation or its anion. To illustrate this, the so-called “membrane potential” at the boundary between a membrane and its surrounding solution was postulated as a consequence of the difference in concentration. In 1911, Donnan [5] confirmed the existence of such boundary and developed a mathematical equation describing the concentration equilibrium, which resulted in the so-called “Donnan exclusion potential”. However, the actual basic studies related ion exchange membranes were firstly begun in 1925 and carried out by Michaelis and Fujita with the homogeneous, weak acid collodium membranes [6]. In 1930s, Söllner presented the idea of a charge-mosaic membrane or amphoteric membrane containing both negatively and positively charged ion exchange groups and showed distinctive ion transport phenomena [7]. Around 1940, interest in industrial applications led to the development of synthetic ion exchange membrane on the basis of phenol-formaldehyde-polycondensation [8]. Simultaneously, Meyer and Strauss proposed an electrodialysis process in which anion exchange and cation exchange membranes were arranged in alternating series to form many parallel solution compartments between two electrodes [9]. It was hard to go into the industrial implications because commercial ion exchange membranes with excellent properties especially low electric resistance were still not available at that time. With the development of stable, highly selective ion exchange membrane of low electric resistance in 1950 by Juda and McRae of Ionics Inc. [10] and Winger et al. at Rohm in 1953 [11], electrodialysis based on ion exchange membranes rapidly became an industrial process for demineralizing and concentrating electrolyte solutions. Since then, both ion exchange membranes and electrodialysis have been greatly improved and widely used in many fields. For example, in 1960s, first salt production from sea water was realized by Asahi Co. with monovalent ion permselective membranes [12]; in 1969, the invention of electrodialysis reversal (EDR) realized long-term run without salt precipitation or deposition on both membranes and electrodes [13]; in 1970s, a chemically stable cation exchange membrane based on sulfonated polytetra-fluorethylene was first developed by Dupont as Nafion[®], leading to a large scale use of this membrane in the chlor-alkali production industry and energy storage or conversion system (fuel cell) [14]; simulta-

neously, a composition of cation exchange layer and an anion exchange layer into a bipolar membrane in 1976 by Chlanda et al. [15] brings many novelty in electrodialysis applications today [16]. Also, stimulated by the development of new ion exchange membranes with better selectivity, lower electrical resistance and improved thermal, chemical and mechanical properties, other applications of ion exchange membranes apart from the initial desalination of brackish water have recently gained a broader interest in food, drug, chemical process industry as well as biotechnology and waste water treatment nowadays [16–23].

Apart from polymeric ion exchange membranes, an ion exchange membrane can also be prepared from inorganic material, such as zeolites, bentonite or phosphate salts [24–26]. However, these membranes are rather unimportant due to their high cost and other disadvantages, such as relative bad electrochemical properties and too large pores though they can undergo higher temperatures than organic membranes [27]. It can be expected that ion exchange membranes prepared from polymers can possess both chemical stability and excellent conductivity if the membranes were incorporated into inorganic components, such as silica. So inorganic–organic ion exchange membrane were developed in late of 1990s by sol–gel for applications in severe conditions, such as higher temperature and strongly oxidizing circumstances [27–29]. Thus, till now, various ion exchange membranes including inorganic–organic (hybrid) ion exchange membranes, amphoteric ion exchange membranes, mosaic ion exchange membranes, bipolar membranes (ion exchange composite membranes) are available and their position in ion exchange membrane development history as well as the important affairs related to them are schematically shown in Fig. 1.

Though ion exchange membranes and the related processes has received multidiscipline attention in both theoretical investigations and industrial applications nowadays, a more recently informative review including all the ion exchange membrane types and synthesis or novel ion exchange membrane-based processes is still insufficient except some reviews on specific aspects, such as modifications of ion exchange membranes [30,31]. Electro-catalytic membrane reactors [32], radiation-induced graft copolymerization for ion exchange membrane preparation [33,34], ion exchange membrane applications [21] or bipolar membrane process and applications in environmental protection [23] and in food industry [24]. Furthermore, ion exchange membrane-related processes are gradually considered less important than pressure-driven membrane processes, such as RO, NF, UF, etc. due to the commercial interests. But they are actually indispensable for separation of ionic species, especially in environmental protection and clean production and in many applications, ion exchange membrane-related processes are in direct competition with other separation techniques, such as distillation, ion exchange and various chromatographic procedures [2]. Therefore, to awaken researcher’s interest in this field and also to understand the present states of

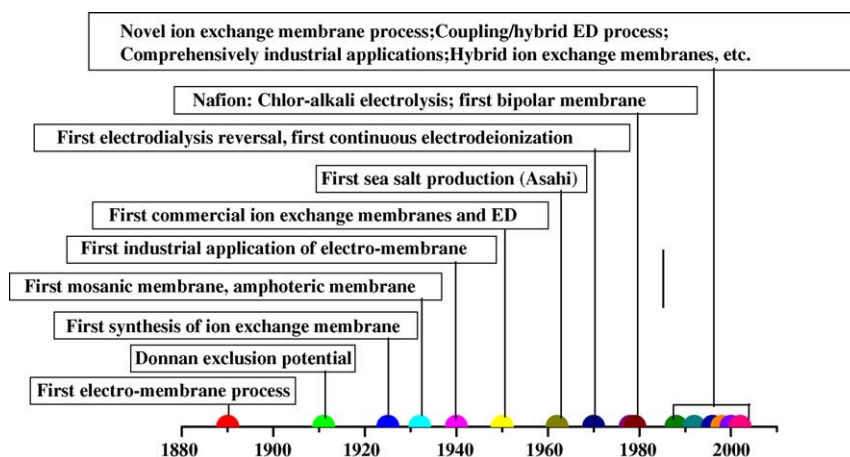


Fig. 1. Time line visualization of ion exchange membrane development and their related processes.

ion exchange membrane research, this review is to give a summary of what have been accomplished in ion exchange membranes and development of novel ion exchange membrane processes. Since extensive work has been reported in the past decade on synthesis, characterization, properties and applications of these membranes, it is difficult to give a comprehensive review of all work accomplished in these areas in a single paper. Thus, this paper is not intended as a review of the literature in these areas. Instead, it is focused on synthesis and some new important applications of major homogeneous ion exchange membranes, hybrid ion exchange membranes, as well as bipolar membranes studied recently with the help of the results obtained in the author's laboratory to illustrate the progress in these areas. The paper will not cover mass transport and the characterizations of these membranes.

2. Homogeneous ion exchange membranes

To prepare homogeneous ion exchange membranes, various approaches are available to introduce ionic groups. These approaches can be classified into three categories based on the starting materials [2,33].

- Starting with a monomer containing a moiety that either is or can be made anionic or cationic exchange groups, which can be copolymerized with non-functionalized monomer to eventually form an ion exchange membrane.
- Starting with polymer film, which can be modified by introducing ionic characters either directly by grafting of a functional monomer or indirectly by grafting non-functional monomer followed by functionalization reaction.
- Start with polymer or polymer blends by introducing anionic or cationic moieties, followed by the dissolving of polymer and casting it into a film.

If the membrane is prepared from monomer, styrene and divinylbenzene are most commonly utilized neutral starting material for a traditional hydrocarbon type ion exchange

membrane for industrial uses, from which a strongly basic anion exchange membrane is usually prepared by two steps, chloromethylation and quaternary amination and the cation exchange membrane prepared by sulfonation. There exist numerous references in the literature for homogeneous ion exchange membrane preparation using such method [2,35–39].

A great deal of work has been dedicated to prepare ion exchange membranes from polymer film. Generally, these polymers are insoluble to any solvents, such as polymer films of hydrocarbon PE and PP or fluorocarbon origin (PTFE, FEP, PFA, ETFE and PVDF). In such route, two functional acidic groups were mainly identified as fixed ionic groups that confer the membrane its cation character, namely carboxylic (weakly acidic) and sulfonic acid (strongly acidic) groups. The former can be prepared either by direct grafting of acrylic monomers like acrylic [40–44], methacrylic acids [45–49] and their mixtures with acrylonitrile [50,51] and vinylacetate [52] or by grafting of epoxy acrylate monomers, such as glycidyl acrylate or glycidyl methacrylate onto polymer films followed by the conversion of the epoxy group into carboxylic group, such as iminodiacetate groups which were obtained by post-grafting ring opening reaction [53]. Strongly acidic membranes are commonly prepared by grafting of styrene onto polymer films and the resulted graft copolymer films are subsequently sulfonated [54–61].

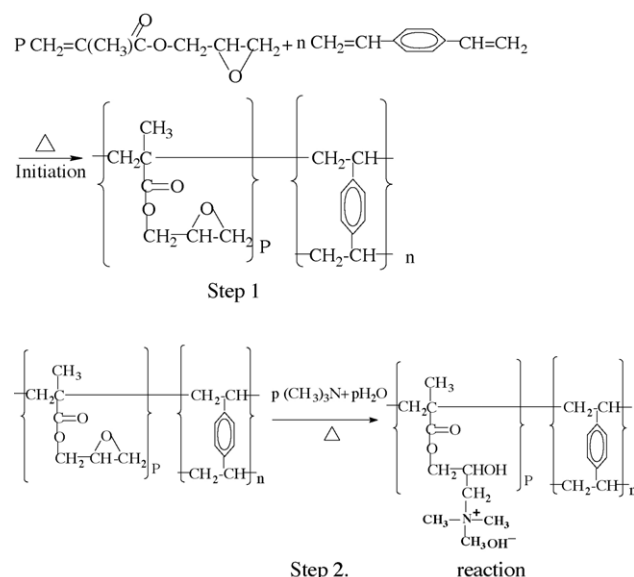
Also, significant efforts have been made to prepared anion exchange membranes from analogous polymer films. The common used method is the same as the second one of cation exchange membrane: grafting vinyl monomers, such as styrene onto polymer films followed by subsequent chemical modifications, such as chloromethylation-amination instead of sulfonation [62,63]. An alternative way is to graft copolymerization of vinyl monomers, such as 4-vinylpyridine, 2-vinylpyridine and vinylbenzylchloride onto various polymer films using various grafting technologies, such as UV-induce, plasma and irradiation methods. Anion exchange functional groups can be either strongly basic, such as tertiary ammonium or weakly basic, such as primary, secondary or tertiary

amine groups. Anion exchange membranes prepared by grafting of 4-vinylpyridine onto films, such as PTFE [64,65], PE [65,66], PP [67,68], ETFE [69], PVDF [70,71], penton [72] and polyvinyl chloride (PVC) [73] followed by quaternization with alkyl halide have been reported in literature.

For soluble polymers, such as PEK, PEK-C, PS, PES or their blends or block copolymers, the membrane can be obtained either by introducing anionic or cationic moieties, followed by the dissolving of polymer and casting it into a film or by dissolving of polymer and casting it into a film, followed by introducing anionic or cationic moieties [74–82]. However, for membrane preparation with soluble polymers, its chemical stability is in doubt and often need post treatment, such as crosslinking with diamine for anion exchange membrane preparation [83].

It is noted that, compared with the cation exchange membrane, preparation of an anion exchange membrane seems to be more complicated and costly, because in the chloromethylation, the common-used chloromethyl methyl ether is a carcinogen and is potentially harmful to human health [84]. Several efforts have been made to avoid the use of chloromethyl methyl ether for preparing anion exchange membranes. Grafting copolymerization of pyridine and its derivative onto polymer films and then quaternization with alkyl halide as mentioned above provide examples of such membranes. The chloromethyl methyl ether can also be avoided by directly grafting vinylbenzylchloride onto polymer films or by copolymerizing with other monomers, such as divinylbenzene (DVB) to form copolymer films that can be converted to anion exchange membrane by simple amination reaction [85–87]. Copolymerization of epoxy acrylate monomers, such as glycidyl acrylate or glycidyl ethacrylate with other monomers, such as divinylbenzene subsequent amination with triethyl amine can serve as alternative route to prepare anion exchange membranes [88]. Scheme 1 presents a reaction route for preparing such anion exchange membrane.

If economy and practice as well as variety in membrane formation have to be considered, chloromethylation by taking advantage of methyl group in available polymers should be the best choice to delete the use of chloromethyl methyl ether. For example, a more simple and practical route for the preparation of anion exchange membranes is shown in Fig. 2 in comparison with conventional anion exchange membrane preparation [89]. In this new route, anion exchange membranes were directly prepared from engineering polymer poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) by bromination instead of chloromethylation with chloromethyl methyl ether. The properties cannot only be quantitatively controlled by position (benzyl substitution or aryl substitution) and content of bromination processes but also be controlled by amination-crosslinking processes [89,90]. It is noted that this crosslinking can be conducted after the formation of base membrane (Fig. 2b), differing from the conventional route (Fig. 2a) in which the base membrane is formed through crosslinking and thus limit the molding of the membrane with



Scheme 1. Anion exchange membrane preparation by ring opening reaction of epoxy group instead of chloromethylation with chloromethyl methyl ether. Step 1, copolymerization reaction. Step 2, quaternary amination reaction.

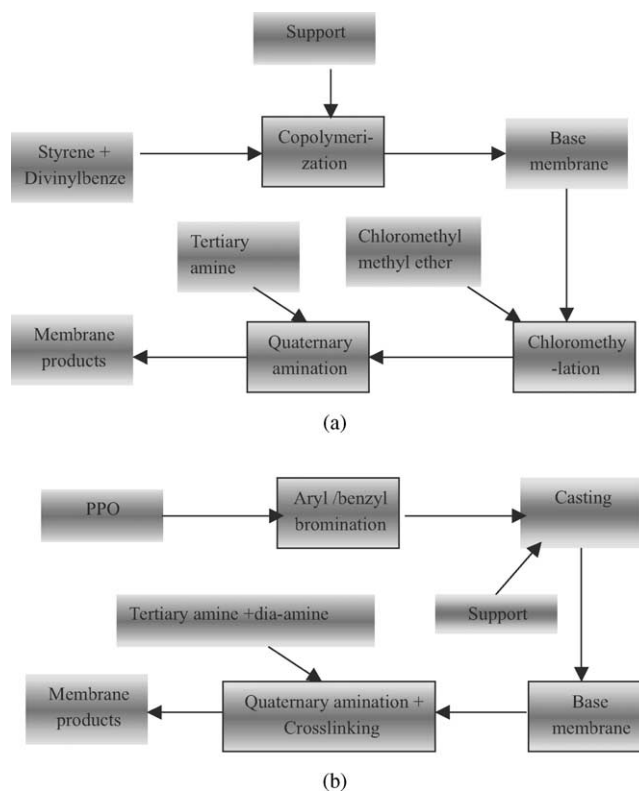


Fig. 2. A comparison manufacture route between conventional hydrocarbon type anion exchange membranes and the anion exchange membranes prepared from polymer poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). (a) Route for a traditional hydrocarbon type anion exchange membrane. (b) Route for a new anion exchange membrane prepared from PPO.

Table 1
Properties of example membrane series developed in this paper^a

Membrane number	ABC ^b (%)	BBC ^b (%)	IEC (mmol/(g dry membrane) (meq/(g dry membrane)))	W _R (g H ₂ O/(g dry membrane))	C _R (M)	R _m (Ω cm ²)	Burst strength (MPa)
1	0.16	0.116	0.89	0.418	2.13	4.82	>0.8
2	0.16	0.173	1.27	0.50	2.52	3.81	
3	0.16	0.285	1.94	0.593	3.26	3.72	
4	0.16	0.310	2.08	0.74	2.80	1.93	
5	0.16	0.328	2.18	0.77	2.82	1.93	
6	0.10	0.285	1.935	0.673	2.87	1.82	>0.8
7	0.28	0.285	1.952	0.478	4.08	3.81	
8	0.38	0.285	1.943	0.442	4.39	4.32	
9	0.42	0.285	1.933	0.387	4.99	4.93	
10	0.54	0.285	1.920	0.302	6.36	5.25	

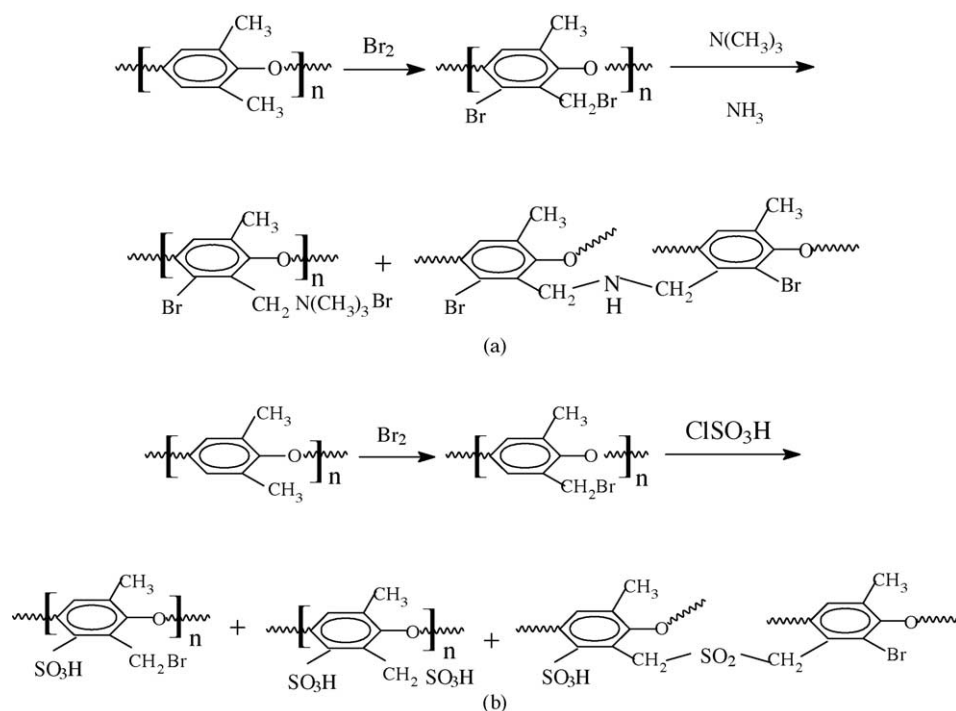
^a All the measurements were conducted at temperature of 25 °C.

^b ABC, aryl bromine content; BBC, benzyl bromine content. Both are assumed mono-substituted.

intricate shape as mentioned above. Using this new route with properly controlling the bromination and amination-crosslinking processes, a series of ion exchange membranes have been initiated and commercially manufactured for diffusional dialysis to recover inorganic acid under different conditions. For example, a membrane with high water content recovers sulfuric acid from titanium white production waste containing sulfuric acid and ferrous ions [91], the analogous membrane with intermediate water content recovers mixed acid (HNO₃ + HF) from titanium leaching liquor [92] and a less hydrated membrane with ammonium aqueous solution simultaneously recovers sulfuric acid and nickel from electrolysis spent liquor of relatively low acid concentration [93]. Membranes of this series have been also used in

electro-dialysis [94], nanofiltration or ultrafiltration [95–97] and anion exchange layer of a bipolar membranes [98], as well as in the separation of different anions [99,100], etc. As an example, Table 1 lists the basic properties of the anion exchange membranes of two catalogues: various aryl substitution with fixed benzyl substitutions or various benzyl substitutions with fixed aryl substitutions [91] and Scheme 2a shows the structure of such anion exchange membranes.

The cation exchange membrane can also be obtained with the same manner: by bromination and sulfonation. The properties can be controlled by content of both bromomethylation and the aryl sulfonation. The typical membranes properties are listed in Table 2 [101,102] and the structure of the cation exchange membrane is shown in Scheme 2b.



Scheme 2. Main reactions and the structure of the ion exchange membrane from PPO. Main reactions and the structure of (a) anion exchange membrane and (b) cation exchange membrane from PPO.

Table 2

Properties of example membrane series developed in this paper^a

Membrane number	BSD ^b (%)	ASD ^b (%)	IEC (mmol/(g dry membrane) (meq/(g dry membrane)))	W _R (g H ₂ O/(g dry membrane))	C _R (M)	R _m (Ω cm ²)	Burst strength (MPa)
1	0.21	0.144	1.07	0.418	2.56	2.82	>0.8
2	0.21	0.155	1.14	0.50	2.28	2.41	
3	0.21	0.163	1.19	0.59	2.02	2.12	
4	0.21	0.188	1.35	0.74	1.82	1.93	
5	0.21	0.287	1.92	0.77	2.49	1.93	
6	0.11	0.285	1.91	0.67	2.85	1.82	>0.8
7	0.18	0.285	1.92	0.58	3.31	2.81	
8	0.32	0.285	1.93	0.52	3.71	3.12	
9	0.45	0.285	1.90	0.49	3.88	2.93	
10	0.69	0.285	1.92	0.46	4.17	3.25	

^a All the measurements were conducted at temperature of 25 °C.^b ASD, aryl sulfonation degree; BSD, benzyl sulfonation degree. Both are assumed mono-substituted.

It should also be pointed out that, poly(phenylene sulfide) (PPS), an analogous polymer to PPO, can also be subjected to the analogous sulfonation for cation exchange membrane preparation. However, since the sulfonated PPS is insoluble in most common solvents, the membrane should be prepared with another polymer, such as polyether ketone (PEK), polyether sulfone (PES), sulfonated polyether ketone (SPEK) or a mixture of them as a binder to produce heterogeneous or semi-homogenous ion exchange membranes [103,104]. Such membrane properties can be further improved by heat treatment of binder polymers [105].

Compared with the ion exchange membrane preparation in labs, the commercialization of ion exchange membranes is indeed insufficiently. The present information on some commercial available ion exchange membranes is tabulated in Table 3 [106,107].

3. Inorganic–organic (hybrid) ion exchange membranes

Inorganic–organic composite materials are increasingly important due to their extraordinary properties within a single molecular composite, which arise from the synergism between the properties of the components [108]. These materials have gained much interest owing to the remarkable change in properties, such as mechanical [109], thermal [110], electrical [111] and magnetic [112] compared to pure organic polymers or inorganic materials. In these materials, organic materials offer structural flexibility, convenient processing, tunable electronic properties, photoconductivity, efficient luminescence and the potential for semiconducting and even metallic behavior. Inorganic compounds provide the potential for high carrier mobilities, band gap tunability, a range of magnetic and dielectric properties and thermal and mechanical stability. In addition to combining distinct characteristics, new or enhanced phenomena can also arise as a result of the interface between the organic and inorganic components [113–115].

Among the many possible applications for inorganic–organic materials, membranes with various compositions and properties are now being prepared from them, especially inorganic–organic (hybrid) ion exchange membranes prepared from inorganic–organic ion exchange composite materials, have received remarkable attentions in recent years. Ion exchange inorganic–organic hybrid membranes can be made by several routes including sol–gel process, intercalation, blending, in situ polymerization, molecular self-assembling, but probably sol–gel process is the most prominent one. For example, Kogure et al. used this method to prepare a hybrid anion exchange membrane by sol–gel or liquid coupling process of silane coupling agents [28]. Through coupling with these agents to silanol group on the surface of silica membranes, the hybrid membranes become insoluble. Further, the inorganic membranes can give enough mechanical strength to the hybrids [28]. The analogous preparation of a hybrid cation exchange membrane was also reported by the same research group [27,29]. Compared with hybrid anion exchange membranes, hybrid cation exchange membranes deserve more attention because the thermal stability of the membranes permits their applications as fuel cell separator [116–124].

Since 2002, preparation of hybrid ion exchange membranes has become one of the major jobs conducted in the author's lab. By incorporating the hybrid material idea into the membranes, various routes for both hybrid anion exchange and cation exchange membranes (materials) were initiated and summarized as the follows.

- (1) The first route for a hybrid (inorganic–organic) anion exchange membrane was prepared through sol–gel process of trimethoxysilyl functionalized PEO-400, i.e., PEO–[Si(OCH₃)₃]₂ and quarternization with C₂H₅Br thereafter. The PEO–[Si(OCH₃)₃]₂ was obtained by end-capping polyethylene oxide (PEO)-400 with tolylene 2,4-diisocyanate (TDI), followed by a reaction with *N*-[3-(trimethoxysilyl) propyl] ethylene diamine (A-1120) as shown in Scheme 3 [125]. The anion exchange capacity

Table 3

Main properties of some commercially available homogeneous ion exchange membranes [106,107]

Membrane	Type	Thickness (mm)	IEC (mol/g (meq/g))	Area resistance (Ω cm ²)	Remarks
Asahi Chemical Industry Co. Japan					
Aciplex K-192	CEM	0.13–0.17	–	1.6–1.9	Univalent selective
Aciplex-501SB	CEM	0.16–0.20	–	1.5–3.0	–
Aciplex A-192	AEM	>0.15	–	1.8–2.1	Univalent selective
Aciplex-501SB	AEM	0.14–0.18	–	2.0–3.0	–
Aciplex A201	AEM	0.22–0.24	–	3.6–4.2	Desalination
Aciplex A221	AEM	0.17–0.19	–	1.4–1.7	Diff. dialysis
Asahi Glass Co. Ltd., Japan					
Selemon CMV	CEM	0.13–0.15	–	2.0–3.5	Strongly acidic
Selemon AMV	AEM	0.11–0.15	–	1.5–3.0	Strongly basic
Selemon ASV	AEM	0.11–0.15	–	2.3–3.5	Strongly basic, univalent
Selemon DSV	AEM	0.13–0.17	–	–	Strongly basic, dialysis
Flemion	–	–	–	–	Chlor-alkali
DuPont Co., USA					
Nafion NF-112	CEM	0.051	–	–	PEM fuel cell
Nafion NF-1135	CEM	0.089	–	–	PEM fuel cell
Nafion NF-115	CEM	0.127	–	–	PEM fuel cell
Nafion N-117	CEM	0.183	0.9	1.5	PEM fuel cell
FuMA-Tech GmbH, Germany					
FKS	CEM	0.090–0.110	0.9	2–4	Standard CEM
FKB	CEM	0.100–0.115	0.8	5–10	For EDBM
FK-40	CEM	0.035–0.045	1.2	1	Proton conductor, thin
FKD	CEM	0.040–0.060	1.0	1	Base dialysis
FAS	AEM	0.100–0.120	1.1	2–4	Standard AEM
FAB	AEM	0.090–0.110	0.8	2–4	For EDBM, acid blocker
FAN	AEM	0.090–0.110	0.8	2–4	Nitrate selective AEM
FAA	AEM	0.080–0.100	1.1	2.4	Base stable
FAD	AEM	0.080	1.3	1.2	Acid dialysis
Ionics Inc., USA					
CR61-CMP	CEM	0.58–0.70	2.2–2.5	11.0	ED whey
CR67-HMR	CEM	0.53–0.65	2.1–2.45	7.0–11.0	ED whey
CR67-HMP	–	–	–	–	EDI
AR103QDP	AEM	0.56–0.69	1.95–2.20	14.5	ED whey
AR204SZRA	AEM	0.48–0.66	2.3–2.7	6.2–9.3	EDR
AR112-B	AEM	0.48–0.66	1.3–1.8	20–28	Nitrate selective
MEGA a.s., Czech Republic					
Ralex MH-PES	AEM	0.55 (Dry)	1.8	<8	ED, EDI
Ralex AMH-5E	AEM	0.7 (Dry)	1.8	<13	Cataphoresis
Ralex CM-PES	CEM	0.45 (Dry)	2.2	<9	ED, EDI
Ralex CMH-5E	CEM	0.6 (Dry)	2.2	<12	Anaphoresis
PCA Polymerchemie Altmeier GmbH, Germany					
PC 100 D	AEM	0.08–0.1	1.2 Quat.	5	Small organic anions
PC 200 D	AEM	0.08–0.1	1.3 Quat.	2	Medium organic anions
PC Acid 35	AEM	0.08–0.1	1.0 Quat.	–	HCl production
PC Acid 70	AEM	0.08–0.1	1.1 Quat.	–	Pickling acids (HNO ₃ /HF)
PC Acid 100	AEM	0.08–0.1	0.57 Quat.	–	Sulphuric acid production
PC-SK	CEM	–	–	–	Standard CEM
PC-SA	AEM	–	–	–	Standard AEM
Solvay S.A., Belgium					
Morgane CDS	CEM	0.130–0.170	1.7–2.2	0.7–2.1	Standard CEM
Morgane CRA	CEM	0.130–0.170	1.4–1.8	1.8–3.0	Reconc. of acids
Morgane ADP	AEM	0.130–0.170	1.3–1.7	1.8–2.9	High demin. or recons.
Morgane AW	AEM	0.130–0.170	1.0–2.0	0.9–2.5 (HCl 1 M)	HCl and HNO ₃ recovery
–	–	–	–	1.3–4.4 (HNO ₃ 1 M)	
Tokuyama Co., Japan					
Neosepta CM-1	CEM	0.13–0.16	2.0–2.5	0.8–2.0	Low R_m
Neosepta CM-2	CEM	0.12–0.16	1.6–2.2	2.0–4.5	Low D
Neosepta CMX	CEM	0.14–0.20	1.5–1.8	2.0–3.5	High strength

Table 3 (Continued)

Membrane	Type	Thickness (mm)	IEC (mol/g (meq/g))	Area resistance ($\Omega \text{ cm}^2$)	Remarks
Neosepta CMS	CEM	0.14–0.17	2.0–2.5	1.5–3.5	Univalent selective
Neosepta CMB	CEM	0.22–0.26	–	3.0–5.0	High strength
Neosepta AM-1	AEM	0.12–0.16	1.8–2.2	1.3–2.0	Low R_m
Neosepta AM-3	AEM	0.11–0.16	1.3–2.0	2.8–5.0	Low D
Neosepta AMX	AEM	0.12–0.18	1.4–1.7	2.0–3.5	High strength
Neosepta AHA	AEM	0.18–0.24	–	3.0–5.0	Base resistant
Neosepta ACM	AEM	0.10–0.13	1.4–1.7	3.5–5.5	Proton blocker
Neosepta ACS	AEM	0.12–0.20	1.4–2.0	3.0–6.0	Univalent selective
Neosepta AFN	AEM	0.15–0.18	2.0–3.5	0.2–1.0	Diff. dialysis
Neosepta AFX	AEM	0.14–0.17	1.5–2.0	0.7–1.5	Diff. dialysis
Tianwei Membrane Co. Ltd., China					
TWEDG	AEM	0.16–0.21	1.6–1.9	3–5	Standard AEM
TWDDG	AEM	0.18–0.23	1.9–2.1	<3	Standard AEM for DD
TWAPB	AEM	0.16–0.21	1.4–1.6	5–8	Proton blocker
TWANS	AEM	0.17–0.20	1.2–1.4	6–10	Nitrate selective AEM
TWAHP	AEM	0.20–0.21	1.2–1.4	<2	High protein flux
TWAEDI	AEM	0.18–0.21	1.6–1.8	6–8	For EDI
TWCED	CEM	0.16–0.18	1.4–1.6	2–4	Standard CEM
TWCDD	CEM	0.16–0.18	1.6–2.0	2–4	Standard CEM for DD
TWCEDI	CEM	0.16–0.18	1.2–1.4	5–8	For EDI

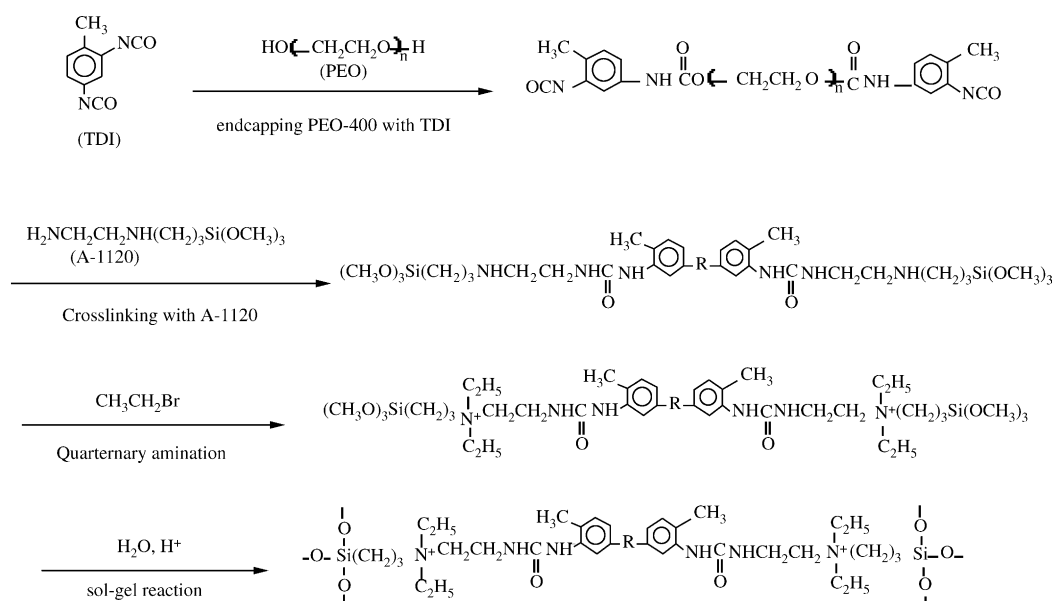
The measurement conditions to determine the area resistance varied with companies: Asahi Chemical Co., 0.5 M NaCl at 25 °C; Asahi Glass Co. Ltd., 1 kHz AC in a 0.5 M NaCl solution; DuPont Co., 0.5 M NaCl at 25 °C; FuMA-Tech, GmbH, 0.6 M NaCl at 25 °C; PCA Polymerchemie Altmeier, GmbH, 1N KCl; Solvay S.A., 1 kHz AC in 10 g/l NaCl at 25 °C, except AW which is measured in a 1 M H₂SO₄, HCl or HNO₃ solution at 25 °C; Tokuyama Co., 0.5N NaCl at 25 °C; Tianwei Co., 0.1N NaCl at 17 °C.

(IEC) was in the range of $(1.6–3.9) \times 10^{-2} \text{ mmol cm}^{-2}$ ($(1.6–3.9) \times 10^{-2} \text{ meq cm}^{-2}$).

- (2) An alternative route to a hybrid anion exchange membrane has been prepared from positively charged PMA–SiO₂ nanocomposites, which was synthesized by the sol–gel process of positively charged alkoxysilane-containing polymer precursors. The precursors were synthesized by coupling different amounts of *N*-[3-(trimethoxysilyl) propyl] ethylene diamine (A-1120) to poly(methyl acrylate) (PMA), followed by a quaterniza-

tion reaction and then hydrolysis and condensation as shown in Scheme 4 [126,127]. As shown in Table 4, anion-exchange capacities of these nanocomposites were shown to be in the range of 0.19–1.20 mmol/g (0.19–1.20 meq/g), increasing with the A-1120 content. The low glass transition temperature ensures the elasticity of the hybrids, while the high T_d endows the thermal stability.

- (3) As described above, modification of PPO is well conducted in our lab for homogeneous ion exchange mem-



Scheme 3. Preparation of PEO–[Si(OCH₃)₃]₂ hybrid anion exchange membrane: R = –NHCOO(CH₂CH₂O)_nCONH–.

Table 4
Thermal properties and anion-exchange capacities (IEC) of PMA–SiO₂ hybrids [126]

	<i>T_g</i> (°C)	<i>T_d</i> (°C)	1000 °C Residue (wt.%) ^a	Practical IEC (mmol/g (meq/g))	Theoretical IEC (mmol/g (meq/g))
PMA–SiO ₂ A	16.8	215	8.4	0.19	0.47
PMA–SiO ₂ B	23.4	196	9.4	0.52	1.05
PMA–SiO ₂ C	20.2	193	12.8	0.56	1.17
PMA–SiO ₂ D	31.5	198	14.0	1.20	2.19

^a Theoretical values based on the assumption that only inorganic moieties are present at 1000 °C.

Table 5
Compositions, thermal properties and anion-exchange capacities (IEC) of hybrid anion exchange membranes (or materials) from bromomethylated PPO(BPPO) [129]

Sample code	The composition of the feed (molar ratio)		The highest decomposition temperature (°C)		IEC (mmol/g BPPO)
	BPPO	A1110	First	Second	
B2A1	2	1	300 (406)	560	1.13
B3A2	3	2	352	561	1.69
B1A1	1	1	356	562	2.97
B1A2	1	2	366	588	4.7

brane. To enhance the thermal properties, a novel hybrid anion exchange membrane was prepared by using bromomethylated PPO as the started polymer. As shown in Scheme 5, the new hybrid membrane was obtained by introducing 3-aminopropyl-trimethoxysilane (A1110), together with trimethylamine (TMA) into bromomethylated PPO and then forming silica networks by sol–gel process through further condensation and hydrolysis reactions with A1110 [128–130]. The main properties of the hybrids are listed in Table 5. It was shown that this series of hybrids could endure a temperature more than 300 °C. IEC values of the hybrids range from 1.13 mmol/g BPPO to 4.7 mmol/g BPPO due to the different feed composition of the hybrid materials.

- (4) The sol–gel process and oxidation of 3-(mercaptopropyl) trimethoxysilane (MPTS, commercial name KH590) in an inorganic support, such as alumina plate provide a convenient route for preparing a cation exchange membrane. The route for this membrane is shown in Scheme 6 [131,132]. The membranes prepared in this manner show that IECs of the membranes increase with an increase of the coating times within a range of $(1.0–2.3) \times 10^{-2}$ mmol cm^{−2} ($(1.0–2.3) \times 10^{-2}$ meq cm^{−2}) for 1–4 coating times. The thermal stability was confirmed by TGA results, which showed that the membranes could

endure a temperature as high as 250 °C. The membranes not only demonstrates the conventional ion exchange capacity, but also can be prepared as nanofiltration or ultrafiltration membrane by properly controlling the coating times and the concentration of sol. For example, after coating 1, 2, 3 and 4 times on the ceramic alumina plate (with pore diameter about 0.2–0.3 μm), the average pore diameter is reduced to the following ranges, 0.1–0.006, 0.056–0.002, 0.051–0.001 and 0.025–0.001 μm for different sol compositions [131].

- (5) The recently initiated route for a hybrid cation exchange membrane is shown in Scheme 7 [133,134]. The Scheme has some similarity to Scheme 3 but phenylaminomethyl triethoxysilane (ND-42) is instead of A-1120 in the crosslinking reaction and sulfonation instead of quaternary amination. The ion exchange capacity of the membrane of material depends not only on the molecular weight of PEO but also on the sulfonation degree. Tables 6 and 7, respectively, show the IECs for various PEO molecular weights and the sulfonation degree. If

Table 6
Dependence of cation-exchange capacities and thermal properties of the hybrid materials prepared on molecular weights of PEO^a [133]

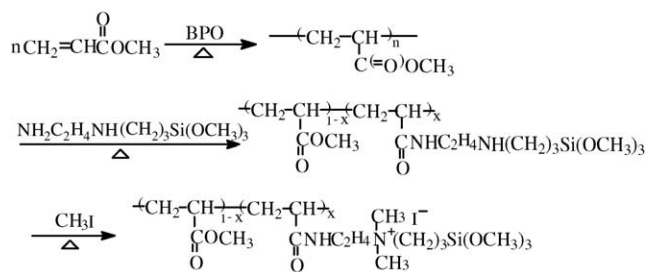
PEO molecular weights	200	400	600	800	1000
IEC (mmol/g)	1.473	1.151	0.666	0.415	0.304
<i>T_d</i> (°C)	239	212	193	191	158

^a Molar ratio of chlorosulfonic acid: PEO–[Si(OEt)₃]₂ is fixed at 6:1.

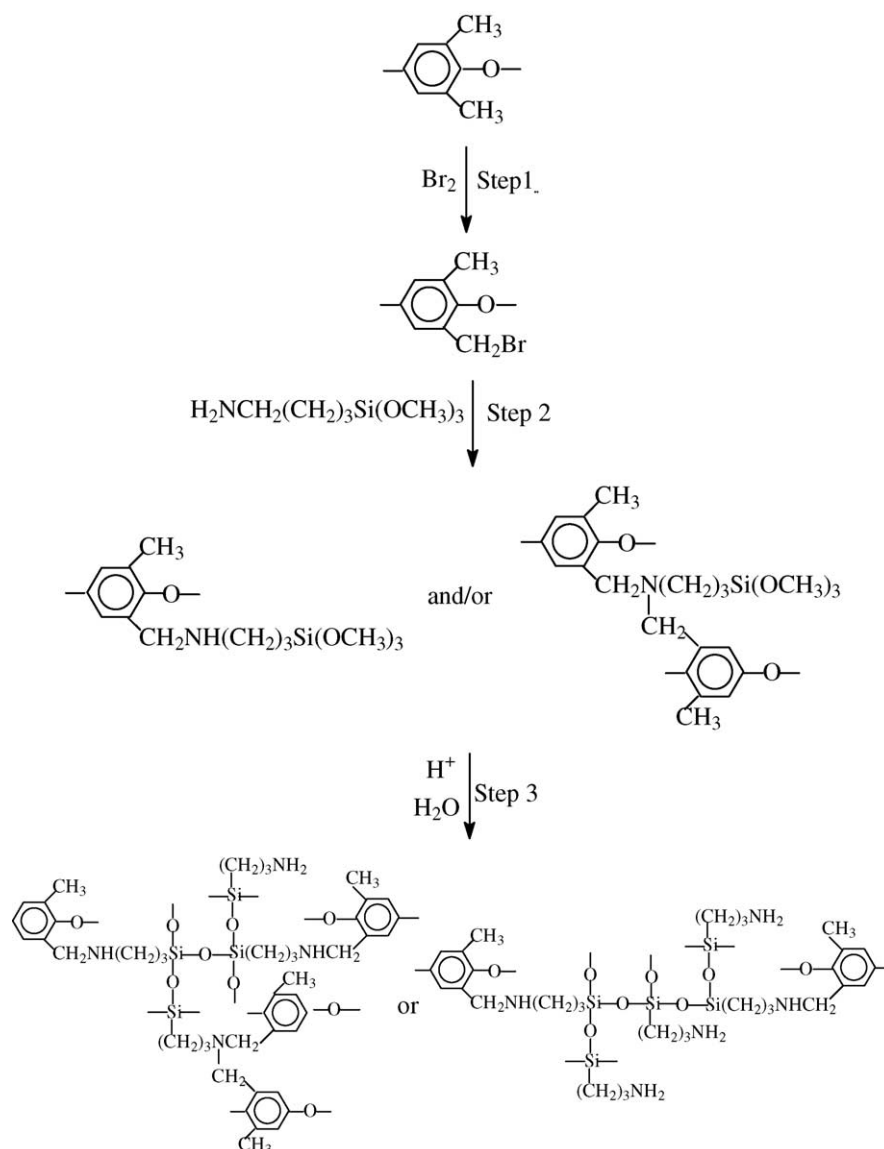
Table 7
Thermal stability, ion exchange capacity (IEC) and water uptake (*W_R*) of hybrid membranes prepared from PEO 1000 with different sulfonation^a [134]

Sulfonation degree	0.23	0.24	0.55	0.56
<i>T_d</i> (°C)	265	261	248	233
IEC (mmol/g)	0.418	0.425	0.976	0.997

^a Molar ratio of chlorosulfonic acid: PEO–[Si(OEt)₃]₂ varied from 1.5:1, 2:1, 4:1 to 6:1, respectively.



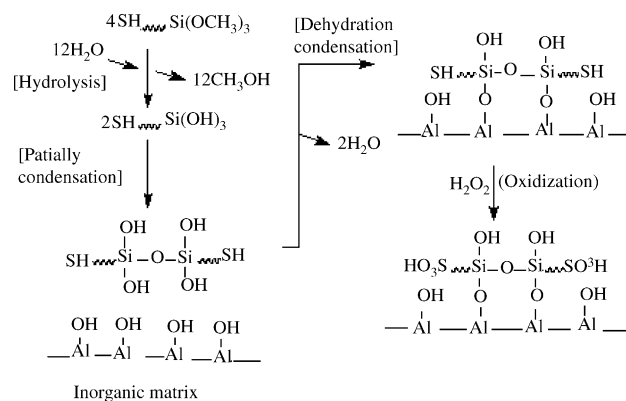
Scheme 4. Preparation of positively charged PMA-A1120 hybrid material and its membrane.



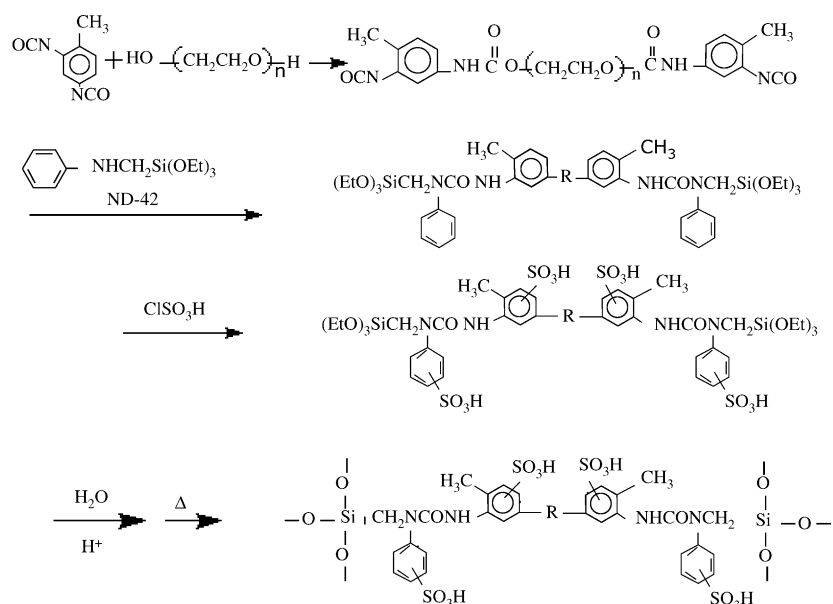
Scheme 5. Preparation of organic–inorganic hybrid anion exchange membrane (materials) based on bromomethylated PPO by sol–gel process. Step 1, bromination of PPO; step 2, synthesis of alkoxy silane-containing polymer precursors; step 3, preparation of organic–inorganic hybrid materials by sol–gel process.

molar ratio of chlorosulfonic acid: $\text{PEO}-[\text{Si}(\text{OEt})_3]_2$ is fixed at 6:1, thermal stability and cation-exchange capacity of the hybrid material decreases with an increase in the molecular weight of PEO; while if the molecular weight of PEO is fixed at 1000, thermal stability declines but cation-exchange capacity is enhanced with an increase in molar ratio of chlorosulfonic acid to $\text{PEO}-[\text{Si}(\text{OEt})_3]_2$. The final membranes can possess T_d s in the range of 265–233 °C, cation exchange capacity in the range of 0.4–1.0 mmol/g, negative streaming potential values even at low pH value, low water flux values ($(0.04\text{--}0.51) \times 10^{-5} \text{ l}/(\text{m}^2 \text{ Pa h})$) and nanoscale pore diameter (0.001–0.004 μm) [134].

In summary, the hybrid ion exchange membrane can be prepared by a variety method. Just like the hybrid material, in which the most important thing is the precursor, the charged



Scheme 6. Mechanism of sol–gel and oxidation processes of KH-590 for a hybrid cation exchange membrane.



Scheme 7. Preparation of PEO-[Si(OCH₃)₃]₂ hybrid cation exchange membrane: R = -NHCOO(CH₂CH₂O)_nCONH-.

precursor is very crucial for hybrid ion exchange membrane. The following steps may be performed by the sol-gel reaction at ambient temperatures, forming metal oxide frameworks by hydrolysis and condensation reactions. The morphologies and properties of the resulting materials are controlled by the reaction conditions and the precursors used [108], consequently they will also influence the properties of ion exchange membranes made from these materials.

4. Bipolar ion exchange membranes

A bipolar membrane (BPM) is a kind of composition membrane that at least consists of a layered ion-exchange structure composed of a cation selective layer (with negative fixed charges) and an anion selective layer (with positive fixed charges). Just the same as the discovery of semiconductor N-P junctions brings about the invention of many new semiconductor instruments, this composition of anionic and cationic exchange layer brings about many novelties [135–140], such as separation of mono- and divalent ions, anti-deposition, anti-fouling, water dissociation, etc. Particularly, electrodialytic water splitting employing bipolar membranes to produce acids and bases from the corresponding salts as shown in Fig. 3 has become a new growth point in electrodialysis industries, and great potentialities exist in industries and daily life, such as chemical production and separation, biochemical engineering, environmental conservation, etc. [16,23,35,141–143]. The involvement of a BPM in these fields can significantly change the features of conventional processes and eliminate potential contamination to the environment [144].

Electrodialytic water dissociation with a bipolar membrane is a very energy-efficient way to produce acids and

bases from the corresponding salts, because the set-up can consist of hundreds of cell units stacked between two electrodes like a conventional electrodialysis. However, there are still severe problems, such as the instability of a bipolar membrane at high overlimiting current density conditions [144]. Therefore, the most crucial aspect of these applications is the bipolar membrane itself. For preparing such membranes, various methods have been initiated, such as preparing directly from commercial cation and anion exchange membranes by adhering with heat and pressure or with an adhesive paste [145], preparing by casting a cation exchange polyelectrolyte solution (or an anion exchange polyelectrolyte solution) on a commercial anion exchange membrane (or on a cation exchange membrane) respectively [146,147], or preparing

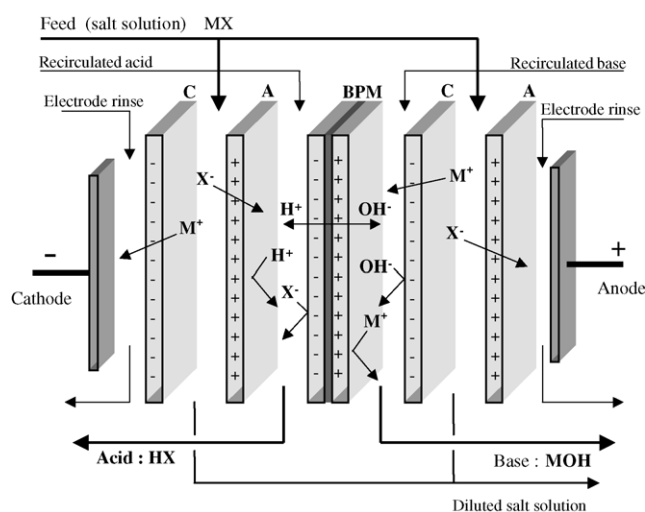


Fig. 3. Electrodialysis with bipolar membranes for the conversion of a salt MX into its respective acid HX and base MOH, taken from Ref. [42].

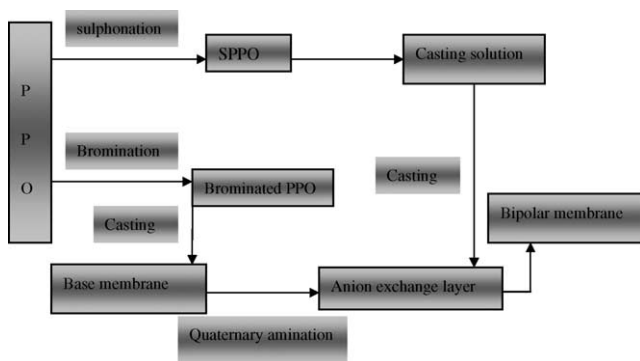


Fig. 4. Schematic diagram of novel bipolar membranes prepared from the same base material poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [98].

from the same base membrane by simultaneous functionalizing at the two membrane sides [148–151] or selectively functionalizing on one side to give cation selectivity and on the other side to give anion selectivity, etc. [152]. Among these, the casting method seems to be the most attractive one for preparing such membranes because it is simple, less costly and also allows a bipolar membrane with desire prosperities for commercial use, such as good mechanical strength, ability to operate at high current density, high permselectivity, low potential drop, etc. [153]. Using this method and the basis of the homogeneous membrane preparation, a novel bipolar membrane has been prepared by casting the sulfonated PPO solution on a series anion exchange membranes as shown in Fig. 4 [98]. Due to the unique structure and same swelling properties in both anion and cation exchange layers, the prepared bipolar membranes possess both excellent mechanical stability and chemical stability [98].

The two ion exchange layers in a bipolar membrane allow for the selective transport of the water dissociation products—protons and hydroxyl ions and block co-ions in the electrolyte. To facilitate the water splitting effect, a bipolar membrane also includes a contact region, also referred to the interfacial layer, where the desired water dissociation reaction occurs. The charged groups and structure of this region are of great significance for water dissociation and thus generally are modified elaborately to improve the bipolar membrane's performance. Now, it is well concluded that materials with the best catalytic activity are sufficient amounts of weak acids (and the corresponding bases), such as amino groups, pyridine, carboxylic acid, phenolic and phosphoric acid group [154–157] as well as heavy metal ion complexes, such as ruthenium trichloride, chromic nitrate, indium sulfate, hydrated zirconium oxide, etc. [158–161]. The catalytic mechanism is underlined by chemical reaction model of water dissociation, that is, the water splitting could be considered as some type of proton-transfer reaction between water molecules and the functional groups or chemicals [156,162]:

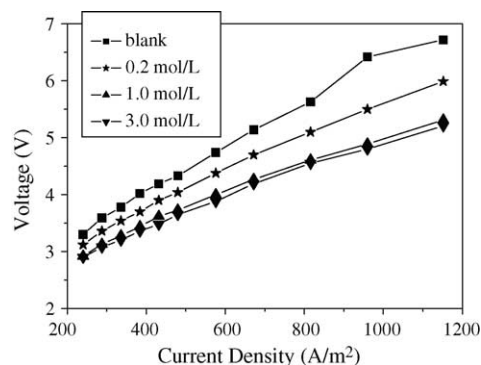
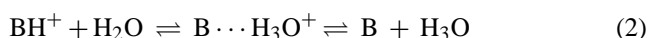
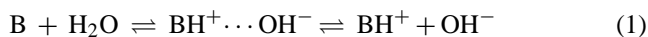
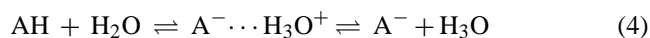
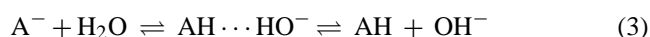


Fig. 5. The I - V curves of bipolar membranes of which the anion exchange membranes have been immersed in different concentration solutions of PEG 2000.

or



where BH^+ and A^- refer to the catalytic centers. The catalytic sites provide an alternative path with low effective activation energy for water splitting into hydrogen and hydroxyl ions.

In order to further elucidate the relationship between the water splitting effect and the chemical composition of the middle layer and to find the varieties in catalyst, current jobs in the author's laboratory are concentrating on using macromolecules, such as polyethylene glycol (PEG) [163], bio-macromolecule bovine serum albumin (BSA) containing both carboxylic and amino groups [164], starburst dendrimers [165], as well as polyvinyl alcohol (PVA) [166] as the interfacial layer to catalyze water dissociation in a bipolar membrane. We have surprisingly found that PEG has greatly improved performance of bipolar membranes from the viewpoint of the I - V curves as shown in Figs. 5 and 6. Further, This catalytic effect not increases with the adsorbed concentration (Fig. 5) but increase with the molecular weight as well (Fig. 6). But for the same material, such as PVA, which has more hydroxyl groups than PEG, the function is much

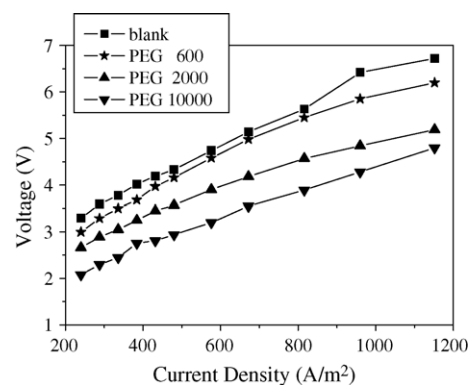


Fig. 6. The I - V curves of bipolar membranes of which the anion exchange membranes have been brushed with 1.0M solutions of different weight of PEGs.

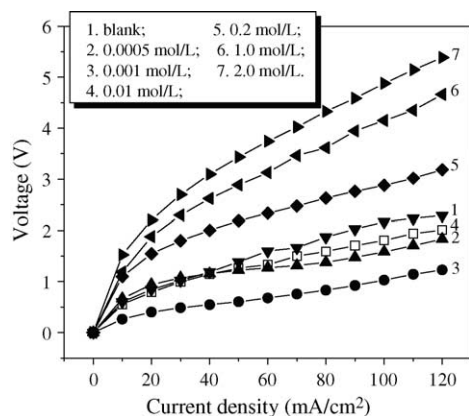


Fig. 7. The I - V curves of bipolar membranes in which anion exchange membranes have been immersed in different concentration PVA solution.

different. As shown in Fig. 7, PVA performs the catalytic effect only at low adsorptional concentration. Theoretical interpretation has been conducted from the aspects of the strong hydrophilicity and interaction of PEG or PVA with water molecules. Though both PEG and PVA are hydrophilic, the hydrogen-bonding and polar interactions between PEG and water molecules are easily formed to increase the solubility of PEG in water, while PVA has a limit in solubility above which it is easily crystallized to give a neutral layer [166].

Another interesting approach reported recently is the modification of a bipolar membrane with the starburst dendrimer polyamidoamine (PAMAM) [165], which possesses much higher amino groups densities than conventional macromolecule as shown in Fig. 8, e.g., a third generation PAMAM prepared from ammonia core has 1.24×10^{-4} amine moieties per unit volume (cubic Angstrom units) in contrast to the 1.58×10^{-6} amine moieties per unit volume contained in a conventional star polymer [167]. As expected, these amino groups of high density in PAMAM have appreciable catalytic function when they are incorporated into the middle layer of a bipolar membrane [165]. However, due to the PAMAM steric effect, the amino groups' catalytic function varies with both PAMAM concentrations and generations. As shown in

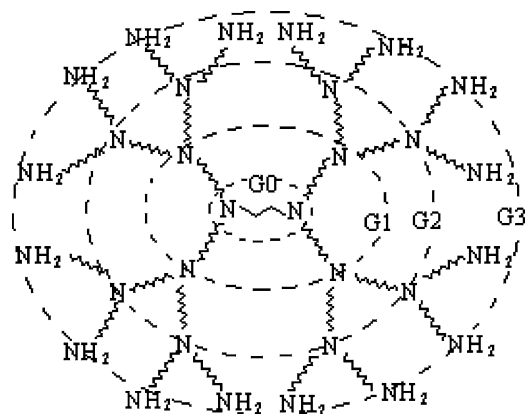


Fig. 8. Schematic diagram of PAMAM G3: the initiate core is ethylenediamine and the repeating unit is $-\text{CH}_2\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{N}-$.

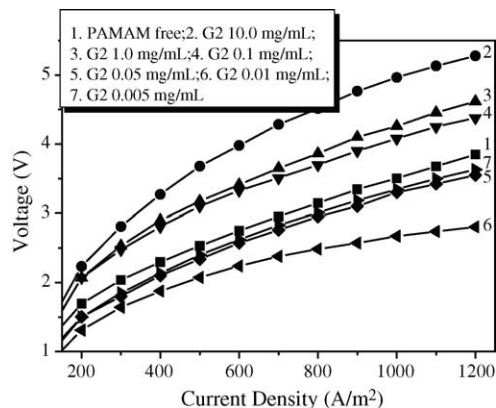


Fig. 9. The I - V curves of bipolar membrane of which the anion exchange membranes have been immersed in different concentration solutions of PAMAM G2.

Fig. 9, at a given PAMAM generation, taking G2 as an example, voltage decreases with PAMAM concentration at low concentration range due to an increase in catalytic sites from amino groups, and increases with PAMAM concentration at high concentration range due to an increase in steric effect. There exists a transitional concentration for each generation of PAMAM. Below this transitional concentration, PAMAM has a catalytic function, above it there is a hindrance effect, and at it the voltage across a bipolar membrane reaches a minimum and the catalytic effect is highest. This transitional concentration decreases with an increase in the generation of PAMAM as demonstrated in Fig. 10, in which voltage dependence on concentration for different generations was plotted at a given current density.

With proper generation and concentration, PAMAM not only work as a catalysis itself, but also can be used to coordinate the heavy metal ions, such as Cr^{3+} , Fe^{2+} that have been found to be effective to water dissociation [139,146,160,168] but easily lost during the operation. As shown in Fig. 11 [169], the voltages cross the bipolar membranes with both PAMAM and $\text{Cr}(\text{III})$ show the minimum among the investigated bipolar membranes without $\text{Cr}(\text{III})$ and PAMAM or with single

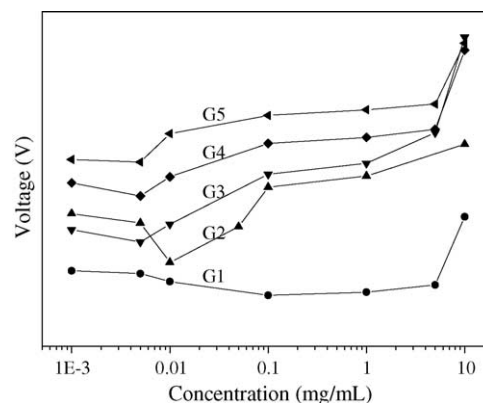


Fig. 10. The relation between the potential drop and the PAMAM concentration at the current density of 1200 A/m^2 .

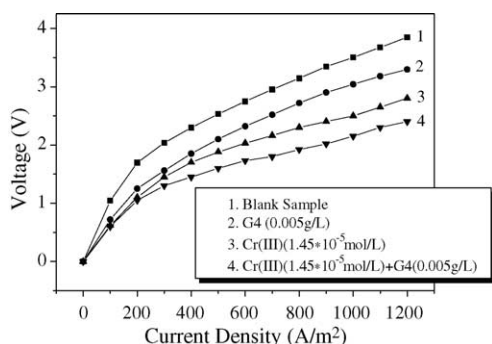


Fig. 11. The I - V curves of bipolar membranes with/without Cr(III) or PAMAM G4.

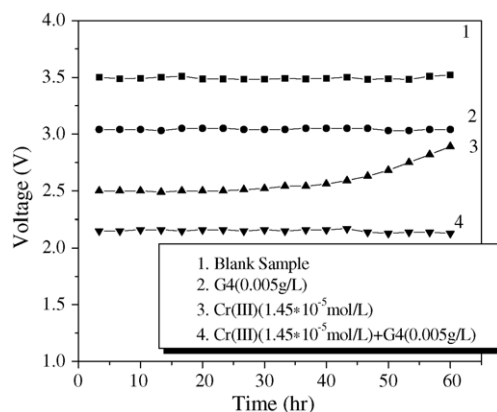


Fig. 12. The V - t curves of bipolar membranes with/without Cr(III) or PAMAM G4.

component Cr(III) or PAMAM, indicating a synergism effect in catalyzing water dissociation. Furthermore, compared with single Cr(III) as an intermediate layer, PAMAM coordinated Cr(III) receive longer catalytic effect as shown in Fig. 12.

Unexpected results were observed for BSA, which contains both carboxylic and amino groups that should enhance the water dissociation according to the chemical reaction model [162]. The experimental results shown in Fig. 13 demonstrated a retardant effect [164]. The reasons are under-

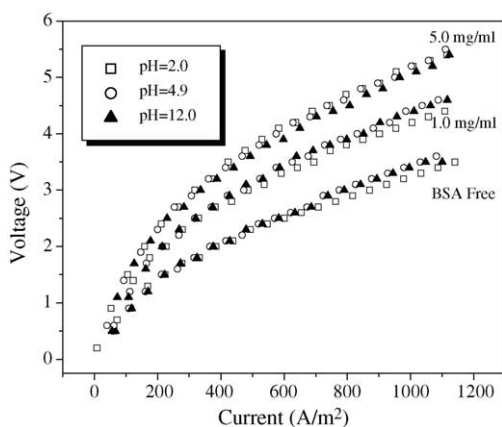


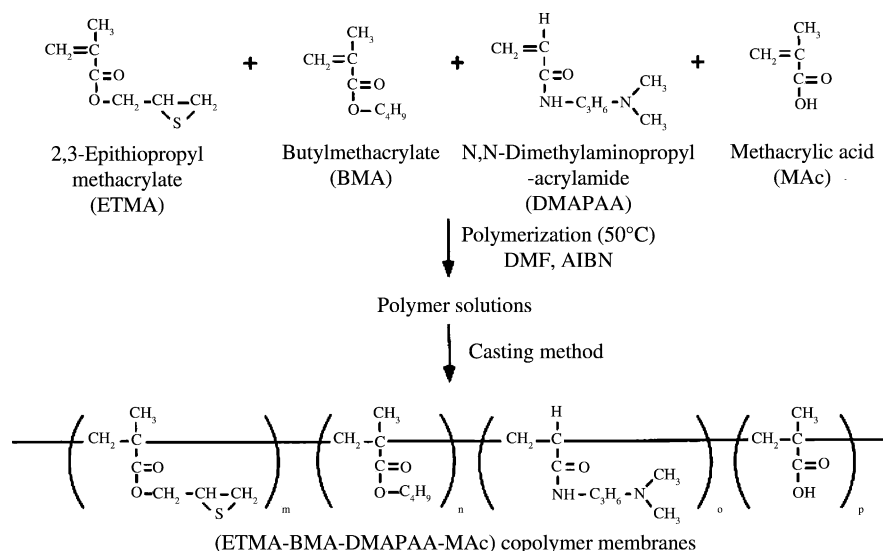
Fig. 13. Effect of BSA in the middle layer on I - V curves at different pH values.

lined by the intrinsic properties of BSA molecules: steric effect gives rise to an increase in the thickness of the depletion layer, its amphoteric property weakens the electric field of the junction and hydrophobicity makes the junction less wettable [164].

Much work has been done in searching for better interfacial layer of a BPM. It is shown that it is easy to synthesize a BPM of small piece with tolerated potential, but it is not so easy to prepared a BPM of larger pieces with longer operational stability at severe circumstances, such as high temperature and over limiting current density [144,146]. The hybrid bipolar ion exchange membrane will be the next choice.

5. Amphoteric ion exchange membranes

Amphoteric ion exchange membranes contain both weak acidic (negative charge) groups and weak basic (positive charge) groups that are randomly distributed within the membrane matrix [7,35,170–173]. The sign of the charge groups in these membranes exhibits a pH response to an external solution. As described earlier, amphoteric ion exchange membranes was first suggested by Söllner in 1932 together with mosaic membranes [7]. Since then, substantial researchers have been conducted for this kind of membrane. For example, Saito et al. [174,175] prepared weakly amphoteric polymer membranes from mixed solutions of poly(vinyl alcohol) and succinyl chitosans composed of carboxy and amino groups as the dissociative groups to determine the interactions occurring between the ion exchange groups on the polyampholyte chain and the counter ions. In the same lab, novel weak porous amphoteric charged membranes having cysteine residues were prepared by graftpolymerising poly(ethylene glycol) derivatives (with cysteine residues added to their side chains) onto a porous cellulose acetate membrane [176]. Nonaka et al. prepared homogeneous amphoteric polymer membranes bearing both amino groups and carboxyl groups from 2,3-epithiopropyl methacrylate (ETMA)-butylmethacrylate (BMA)- N,N -dimethylaminopropyl acrylamide (DMAPAA)-methacrylic acid (MAc) copolymers [177]. The diffusive permeability of solutes with different charged conditions, and the changes in the membrane potential during the permeation of solutes through the amphoteric polymer membranes was investigated. As an example, Scheme 8 shows this membrane structure and preparation route. In addition, Matsuyama et al. studied the permeability of ionic solutes through a polyamphoteric membrane [178]. Ramirez et al. [179] have studied theoretically the effects of pH on the ion transport through amphoteric polymer membranes composed of weak polyelectrolytes. Takagi and Nakagaki [180] theoretically discusses the permeation of ions through the amphoteric membrane using the advanced amphoteric membrane model shown in Fig. 14 and determines the membrane charge by the dissociation of the amphoteric membrane material as well as the selective adsorption of ions.



Scheme 8. Preparation route and structure of amphoteric membrane from (ETMA-BMA-DMAPAA-MAC) copolymer, taken from Ref. [177].

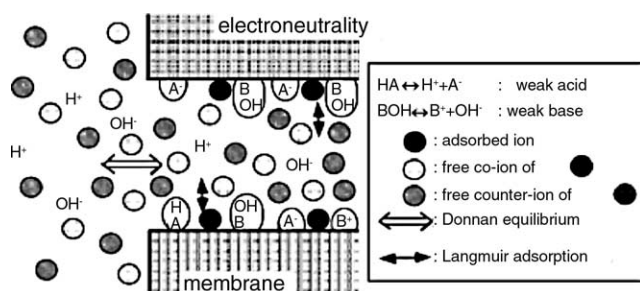


Fig. 14. Advanced amphoteric membrane model, taken from Ref. [180].

Amphoteric charged (ion-exchange) membranes are expected to be the next-generation ion exchange membranes for the following features: controllability of the charge property by changing the pH of the outer solution and their potential as an anti-fouling material that prevents adsorption of organic molecules and biological macromolecules on the surface [181]. They are expected to be utilized in the biomedical and industrial fields, such as medical devices (e.g., hemodialysis membrane) [182–184], separation of ionic drugs and proteins [181,185–188] and depletion of electrolytes by nanofiltration [189] or piezodialysis [190–193] as well as high performance gel actuator [194].

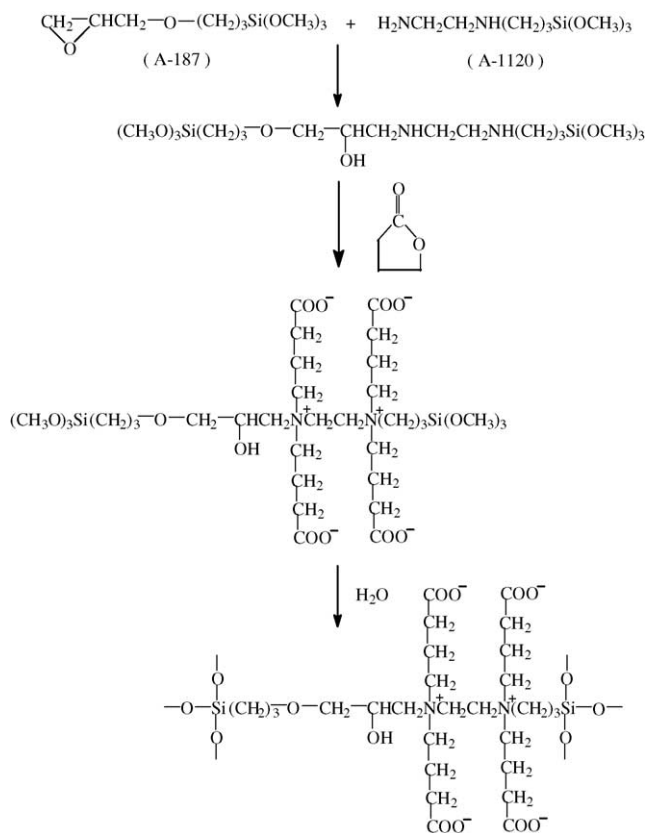
6. Mosaic ion exchange membranes

Differentiating from amphoteric charged membrane with negatively fixed ions and those with positively fixed ions randomly distributed in a neutral polymer matrix, a charge-mosaic membrane consists of a set of anion and cation exchange elements arranged in parallel, each element providing a continuous pathway from one bathing solution to the other [7,35]. When a gradient of electrolyte concentration is established across the membrane, anions and cations

can flow in parallel through their respective pathways without a violation of macroscopic electroneutrality, resulting in a circulation of current between the individual ion-exchange elements. As a result of current circulation, the charge-mosaic membrane shows negative osmosis and salt permeability much greater than its permeability to non-electrolytes; these effects are not displayed in mono-ion exchange membranes or neutral membranes [195,196].

Since Söllner presented the idea of a charge-mosaic membrane in 1932 [7], many efforts have been made to fabricate it. For example, Weinstein and Caplan reported interesting selective transport phenomena for organic and inorganic solutes with a membrane prepared by embedding both cation- and anion-exchange resin powders in silicone rubber [197]. Leitz et al. showed a considerably large salt enrichment with a membrane prepared by the method described as “latex-polyelectrolyte” fabrication [198]. Fujimoto et al. succeeded in fabricating a charge-mosaic membrane made with a well-defined domain structure and tough texture from pentablock copolymers, such as poly(isoprene-*b*-, -styrene-*b*-, -butadiene and -(4-vinylbenzyl) dimethylamine-*b*-isoprene and poly(isoprene-*b*-styrene-*b*-isoprene-*b*-(4-vinylbenzyl) dimethylamine-*b*-isoprene) [199,200]. To modulate the structure of a mosaic membrane, Kawatoh et al. prepared a charge-mosaic membrane from the solution-cast film of the polymer blend of chloromethyl polystyrene (CMPS) with poly(acrylonitrile-co-styrene) (SAN) [201]. To increase the flux for possible industrial applications, recently, Linder and Kedem prepared a asymmetric ion exchange mosaic membrane by solution blends of sulfonated polysulfone (SPSu) and bromomethylated poly(2,6-dimethyl phenylene oxide) (BrPPO), in which the SPSu forms the membrane matrix and the PPOBr ultimately forms the spherical anionic exchange domains within the matrix [202].

By incorporating the idea of hybrid membrane into mosaic ion exchange membranes, recently, a novel route



Scheme 9. Possible reactions of synthesis of hybrid mosaic ion exchange membrane (non-stoichiometric balance).

for a hybrid mosaic ion exchange membrane was proposed in the author's lab [203,204]. The route started from a charged hybrid precursor, which was obtained by a reaction of 3-glycidypropyltrimethoxysilane (GPTMS) with *N*-[3-(trimethoxysilyl) propyl] ethylene diamine (TMSPEDA), and then reacted with γ -butyrolactone (γ -BL) to create ion pairs in the polymer. It was surprisingly found that when the molar ratio of GPTMS:TMSPEDA: γ -BL = 1:1:1, the membrane demonstrated particular molecular structure, in which only one ion pair grafted onto the main chain was arranged in parallel each other, namely, hybrid mosaic ion exchange membrane could be obtained in this way [203]. The step reactions for such membrane are shown in Scheme 9 and the preparation route is shown in Fig. 15.

The hybrid mosaic ion exchange membrane can also be obtained in a more simple and practical way. Scheme 10 shows the recent-developed route for hybrid mosaic charge membrane in the author's lab via coupling reaction of mixed PAMTMS/ $\text{Ti}(\text{O}-n\text{Bu})_4$ modified by Acac as well as zwitterionic process [205]. Two main steps are concerned with this preparation. Firstly, the hybrid precursors are formed through alcoholysis and condensation reaction of phenylaminomethyl trimethoxysilane (PAMTMS) and titanium alkoxide ($\text{Ti}(\text{O}-n\text{Bu})_4$). Then, the positively charged and negatively charged groups are formed through zwitterionic process of the hybrid precursors.

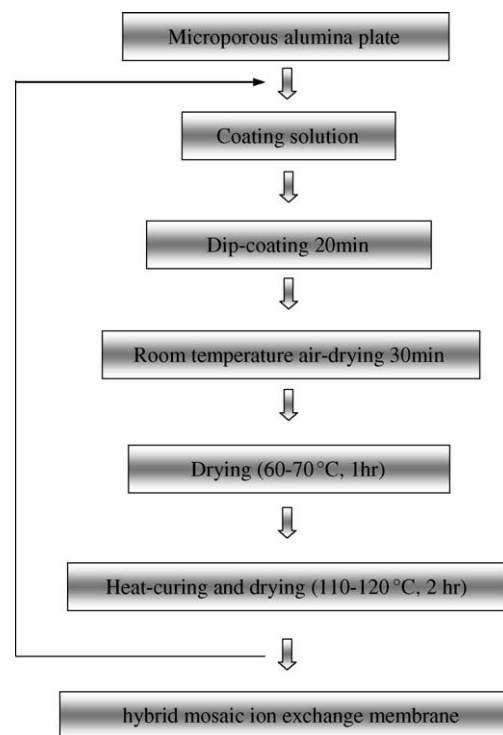
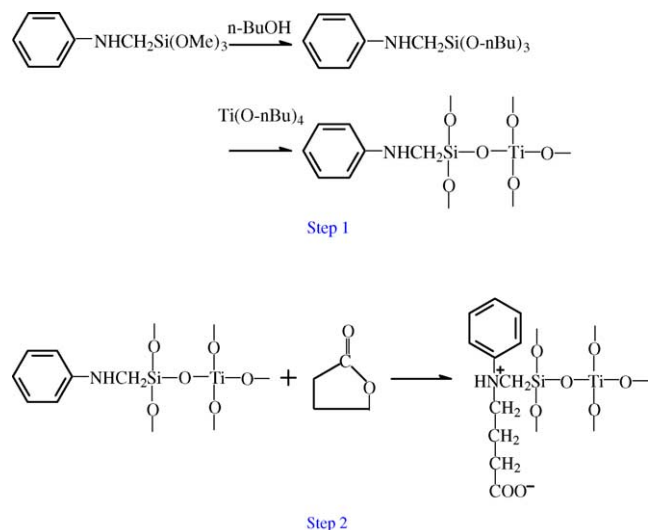


Fig. 15. Procedure for the preparation of hybrid mosaic ion exchange membrane.

To sum up, there are many ways to a mosaic ion exchange membrane. Although common ion exchange membranes are widely found in industrial applications, commercial ion exchange mosaic membrane is still not available. Many fabrication methods are not deemed to be well suited for the industrial production of a charge-mosaic membrane which



Scheme 10. A simple way to synthesis of hybrid charged mosaic membrane through a coupling reaction and zwitterionic process. Step 1, alcoholysis and condensation reaction of phenylaminomethyl trimethoxysilane (PAMTMS) and titanium alkoxide ($\text{Ti}(\text{O}-n\text{Bu})_4$). Step 2, zwitterionic process of the hybrid precursors to create both positively and negatively charged groups.

requires a thin selective layer, optimum domain size, no interfacial leaks between the domains, mechanical strength, ease of preparation and the ability to upscale. Mosaic membranes give unique properties of negative salt rejection or osmotic pressure which may be usefully applied to different separation problems, such as the separation of salts from water-soluble organic substances, treatment of waste streams from dye, food, dairy, fermentation, agriculture, pharmaceuticals and mining industries [202], so further membrane improvements should deserve much attention for general industrial use.

7. Novel processes based on ion exchange membranes

The conventional ion exchange membrane-based processes include electrodialysis, diffusional dialysis and Donnan dialysis, which are used today in a large variety of applications from water desalination, waste water treatment to chemical reactors. Detail descriptions of those applications can be found in some books and reviews [2,3,21,32,33,206]. Especially, a comprehensive analysis on these applications have been made by Strathmann in his recent book [35] and reproduced here in Table 8.

Apart from traditional ion exchange membrane-based processes, in the past decades, numerous novel ion exchange membrane developing processes or to-be-developed ones have been studied, both on a laboratory and on a pilot-plant scale, and new applications in the biomedical, food and energy resources industries have been identified. Some of them have gained increasing attention as efficient techniques in clean production and wastewater treatment [23,35,207].

Electrodeionization (EDI), which is a combination of electrodialysis with conventional ion-exchange technology and proposed in 1970s [208,209], nowadays become a commercially successful technology for the production of ultra-pure deionized water and has been of great necessity in electrical, medical, biological industries. The principle of the process is illustrated as Fig. 16 [21,210], a mixed-bed ion exchange resin or fiber is placed into the diluate cell of a conventional electrodialysis cell unit. The function of the resins is to increase the conductivity in the substantially non-conductive water. At very low salt concentrations, the feed solution water is dissociated at the contact region of the cation- and anion-exchange resin beds, generating protons and hydroxyl ions that further replace the salt ions in the resins. The final result is completely deionized water as the product. The process can be performed continuously without chemical regeneration of the ion-exchange resin. The only disadvantage of the process is the relatively poor current utilization, which can, however, be tolerated in most applications.

Another interesting application of ion exchange membranes is the so-called electrochemical-ion exchange. In this process, an ion exchange membrane is bonded directly on the surface of a metal mesh electrode. By applying a suit-

Table 8

Industrial application of conventional electrodialysis (ED), diffusional dialysis (DD) and Donnan dialysis (DonD) [35]

Industrial applications	Stack and process design	Status of application	Limitations	Key problems	Process
Brackish water desalination	Sheet flow, tortuous path stack, reverse polarity	Commercial	Concentration of feed and costs	Scaling, costs	ED
Boiler feed water production	Sheet flow, tortuous path stack, reverse polarity	Commercial	Product water quality and costs	Costs	ED
Waste and process water treatment	Sheet flow stack, unidirectional	Commercial	Membrane properties and costs	Membrane fouling	ED
Ultra pure water production	Sheet flow, tortuous path stack, reverse polarity	Commercial	Product water quality and costs	Membrane biofouling	ED
Demineralization of food products	Sheet flow, or tortuous path stack, unidirectional	Commercial or pilot phase	Membrane selectivity and costs	Membrane fouling, product loss	ED
Table salt production	Sheet flow stack, unidirectional	Commercial	Costs	Membrane fouling	ED
Concentration of reverse osmosis brine	Sheet flow stack, unidirectional	Pilot phase	Costs	Waste disposal	ED
Separation/recovery of acid/base from its salt solutions	Sheet flow stack, hollow fiber module or spiral module; counter current flow	Commercial	Concentration of products, membrane selectivity, costs	Waste disposal	DD
Water softening, removing heavy metal ions from waste water	Sheet flow stack, hollow fiber module or spiral module; counter current flow	Pilot phase	Costs, limited applications, concentration of feed	Waste disposal	DonD

refers to the case of producing itaconic acid using BMED (Fig. 17a) in comparison with conventional fermentation process (Fig. 17b) [35]. As well known, during the fermentation of itaconic acid, the pH in the fermentation broth shifts to lower values due to the production of the acid. To avoid product inhibition, the pH-value of the fermentation broth is maintained at a certain level by addition of sodium or ammonium hydroxide which reacts with the itaconic acid and forms a soluble salt. In the conventional batch type fermentation process illustrated in Fig. 17a, the spent medium is separated from the biomass by filtration and the free acid is recovered by lowering the pH-value. The pH-value adjustment in the fermenter as well as in the spent medium creates a substantial amount of salts mixed with the product, which complicates the final purification of the itaconic acid and gives rise to an additional waste disposal problem. By integrating bipolar membrane electrodialysis, the production of additional salts in the fermentation broth can be eliminated and the fermentation and thus the production of itaconic acid can be carried out more efficiently in a continuous process as illustrated in the simplified flow diagram of Fig. 17b.

Production of sodium methoxide is an example of BMED used in non-aqueous system [219]. Such application is illustrated in the schematic diagram of Fig. 18, which shows an electrodialysis stack with a bipolar membrane in a repeating unit consisting of two compartments between two electrodes [35,219]. Water-free methanol and sodium acetate are fed into the cell formed by the bipolar membrane and the cation exchange membrane, which is directed towards the cathode while water-free methanol is fed into the other cell directed towards the anode. Due to an electrical potential gradient between the electrodes, methanol is dissociated in the bipolar membrane into protons and CH_3O^- -ions. The proton forms acetic acid with the acetate ions while the CH_3O^- -ions react with the Na^+ -ions, which migrate from the adjacent sodium acetate containing cell and form CH_3ONa . Thus, sodium acetate and methanol are converted to sodium methoxide and

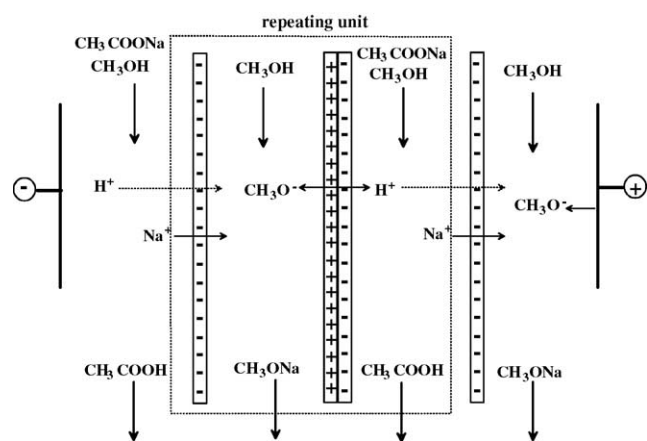


Fig. 18. Schematic drawing illustrating the production of sodium methoxide by electrodialysis with bipolar membranes from methanol using sodium acetate as electrolyte [35,219].

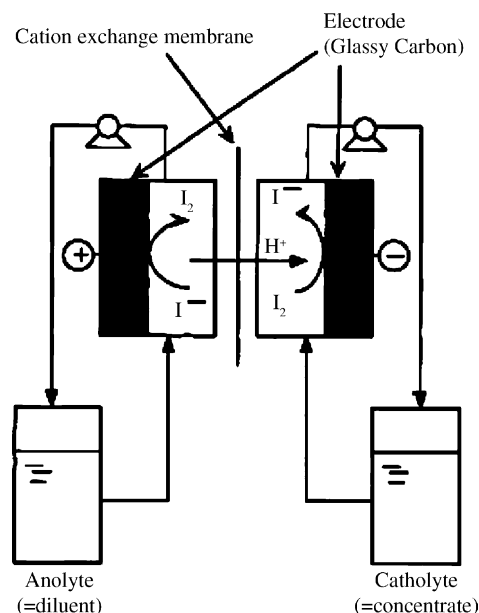


Fig. 19. Concentrating HIX solution with EED based on cation exchange membrane, taken from Ref. [221].

acetic acid. The significance of this process is not only for production of sodium methoxide itself but also in turn provides cheap chemicals for various syntheses, such as the Claisen condensation and the intramolecular Dieckmann condensation reactions, which need alkali alkoxides [220]. By means of BMED, such syntheses can be very environmentally-benign, e.g., production of acetoacetic ester proposed by Sridhar and Feldmann [220].

Electro-electrodialysis (EED) is a combination of electrolysis and electrodialysis with ion exchange membranes. Unlike electrodialysis, which simultaneously needs both cation exchange membranes and anion exchange membranes placed in series, EED only needs a single membrane: either anion exchange membrane or cation exchange membrane. As an example, Fig. 19 illustrates the process of concentrating HIX solution with EED based on a cation exchange mem-

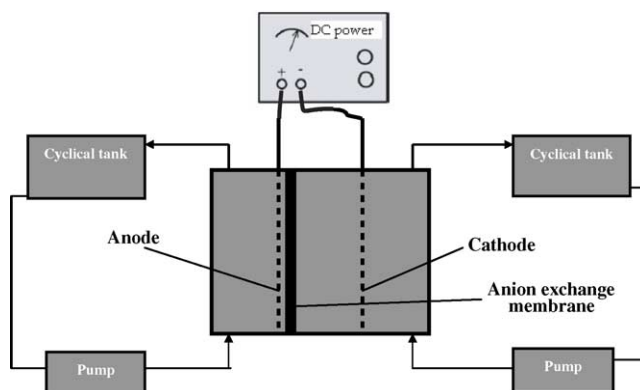


Fig. 20. Electro-oxidation of cerium(III) to cerium(IV) and simultaneous deposition of copper powder on cathode by EED with an anion exchange membrane.

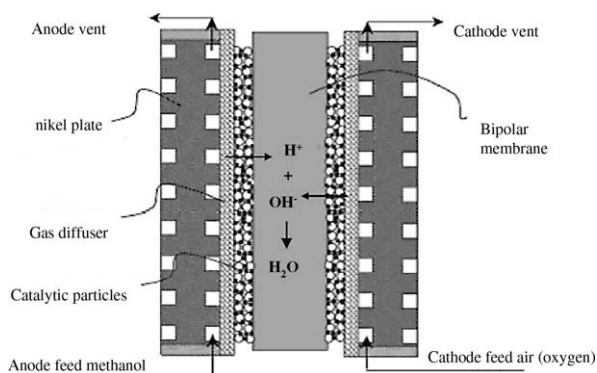


Fig. 21. Schematic representation of methanol direct-conversion fuel cell with a bipolar membrane as polymer electrolyte, adapted from Ref. [32].

brane [221]. In HIX solution, the electrode reaction was the redox reaction of iodine–iodide ions as shown in Fig. 19. Consequently, with the help of selective proton permeation through the membrane, it is expected that the aimed “concentration” is possible in the sense that HI molality of catholyte increases while that of anolyte decreases [221]. Another example for EED with an anion exchange membrane is for the electro-oxidation of cerium(III) to cerium(IV) and simultaneous deposition of copper powder on cathode [222]. As shown in Fig. 20, anolyte is cerium(III) sulfate solution and catholyte is copper sulfate solution. With the passage of an electrical current, cerium(III) oxidizes to cerium(IV) at the anode with the reaction:

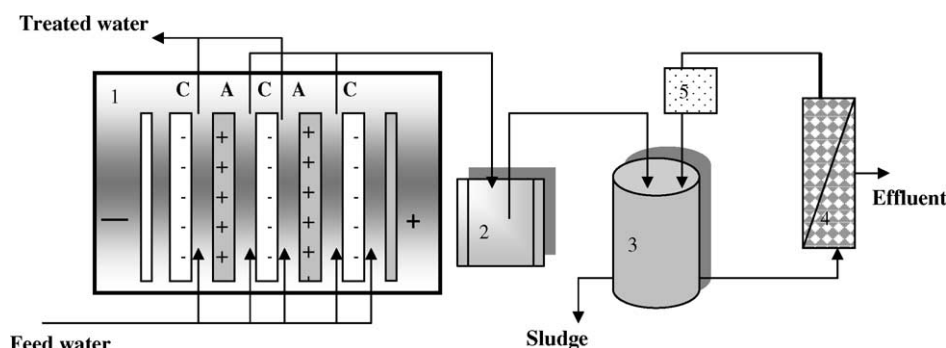


Fig. 22. Schematic diagram in denitrification of drinking water by the association of an electrodialysis (ED) process and a membrane bioreactor (MBR), adapted from Ref. [225]. 1, ED stack; 2, MBR feed tank; 3, fermentor; 4, ultra-filtration module; 5, temperature regulator; C, cation exchange membrane; A, anion exchange membrane.

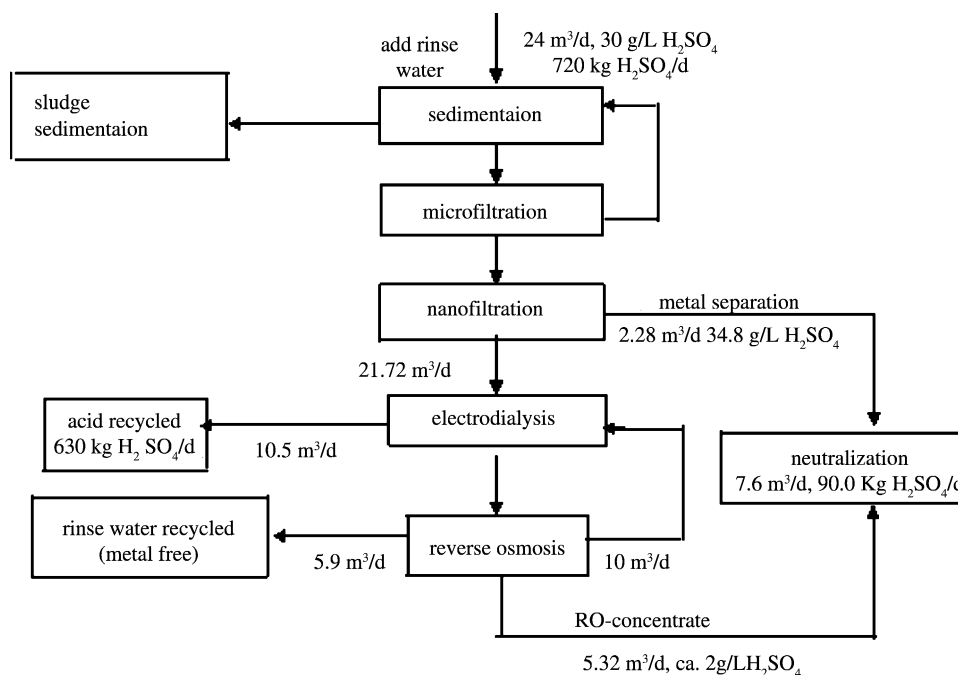


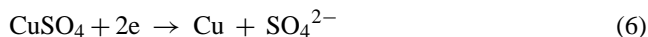
Fig. 23. Process scheme illustrating the treatment and recycling of spent rinse water from a lead/acid battery production line, taken from Ref. [35].

Table 9

Potential applications of novel ion exchange membrane-based process, their state of development and possible advantages and experienced problems [35]

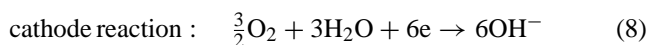
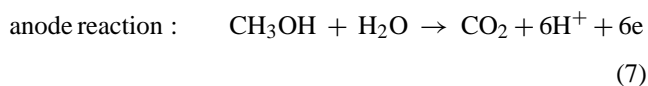
Applications	State of process development	Potential advantages	Problems related to application
Electrodialysis with bipolar membranes (BMED)			
Production of mineral acids and bases from corresponding salts	Pilot plant operation	Lower energy consumption	Contamination of products and low current utilization due to poor membrane permselectivity
Recovering/producing of organic acids from fermentation processes	Commercial and pilot plant operation	Simple integrated process, lower costs	Unsatisfactory membrane stability and fouling application experience.
Removal of SO ₂ from flue gas	Extensive pilot plant test	Decreased salt production, reduced salt disposal costs	High investment costs, long-term membrane stability
Recovering and recycling of H ₂ SO ₄ and NaOH from waste waters, such as the rayon production effluent	Laboratory and pilot plant tests, some commercial plants	Purity of the recovered products is not critical, savings in chemicals and sludge disposal costs	No long-term experience, membrane stability under operating conditions, membrane fouling, high investment costs
Recycling of HF and HNO ₃ from steel pickling solutions	Commercial plants	Cost savings due to recovered acids and decreased salt disposal	Relatively complex process, high investment costs
In food industry	Laboratory and pilot plant tests	Fewer by-products, less chemicals, and salt production and disposal	Application experience, process costs, investment costs
Energy storage and conversion	Only theoretical considerations	Eventually economical advantages	No experimental verification
Production of sodium methoxide from methanol	Laboratory tests	More economic than conventional production process	No long-term experience
EDI			
Ultra-pure water production	Commercial plants	Continuous process without by-products, high efficiency	Higher investment costs, waste disposal, care pretreatment
EED			
Membrane electrolysis	Commercial plants	Continuous process, high efficiency	High investment costs, membrane stability and selectivity
ED and reactor			
Denitrification of drinking water, fermentation process	Pilot plant tests, some commercial plants	Continuous process, high efficiency	Membrane stability and selectivity, relatively complex process
ED and filtration			
Waste recovery	Commercial plants	Continuous process, more compacted process	Relatively complex process, connection with care for each process

And simultaneously copper deposits on the cathode with the reaction:

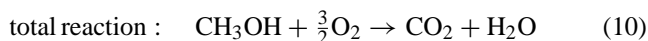


The function of the anion exchange membrane is to let the SO_4^{2-} transport from cathode chamber to anode chamber to balance charges. Apart from these examples, EED is a potential technology for electrochemical reaction in many industries, especially in hydrometallurgy industry [222].

The most important potential large-scale application of ion exchange membrane is their use as separators in fuel cells and batteries. Though Nafion series membranes have been specially designed for this purpose, its high cost and high hydrogen or methanol leaching increase the instability of the related industries [21,32]. Recently, a bipolar membrane is used as proton-conductive polymer electrolyte in the methanol direct-conversion fuel cell [223]. The principle is shown in Fig. 21. An introduction of a bipolar membrane instead of a proton-conductive membrane changes the reaction process:



neutral reaction in bipolar membrane :



The total reaction (10) is completely the same as that in conventional methanol direct-conversion fuel cell based on Nafion membranes or other mono-polar proton transfer membranes, but the advantages are obvious: (1) no water will be produced in the cathode; (2) the cathode reaction was conducted at the base condition, making the cathode cheap and abundant in materials; (3) the protons produced at the anode can not reach the cathode but combine with the hydroxyl ions produced from the cathode, this preventing methanol from leaching through the electrolyte to a great extent. It can be expected that such a fuel cell can attain higher efficiency. However, there is a long way to methanol direct-conversion fuel cell with bipolar membranes before enough fundamental investigations on the water balance, process control, heat balance and the membrane stability.

Another interesting application, which is presently studied, is the integration of ion exchange membrane in the so-called membrane reactors. Fig. 22 shows such integration applied for the treatment of drinking water with high nitrate concentration [224,225]. The ground water contaminated by nitrate resulting from various agricultural and farm activities were first treated by electrodialysis and concentrated brines were then treated by a membrane bioreactor (MBR).

The results showed that the MBR allowed efficient denitrification of ED concentrates despite the drastic conditions of nitrate concentration, pH and salinity. The nitrate concentration of ED dilutes remained below the acceptable value (50 mg/l) and could be drinkable [224,225]. In addition, in many chemical and biochemical reactions, the reaction products or the reaction by-products inhibit the reaction when a certain concentration is exceeded. This often limits the achievable product concentration and requires additional separation and concentration steps. A continuous removal of the reaction inhibiting components often makes a continuous more economic production possible.

A more comprehensive integration of electro-membrane process with press-driven membrane separation processes can be found in the recovery and recycling of water and H_2SO_4 from the rinse solution of a lead battery production line that was developed by Osmota GmbH, Germany [35]. Such integration consisted of several of processes including electrodialysis, microfiltration, nanofiltration and reverse osmosis. The flow scheme of the treatment process is indicated in Fig. 23 together with material balance at each treatment step [35].

Actually, it is hard to list all the developing or to-be-developed ion exchange membrane-based process in this paper. As a summary of this section, Table 9 lists state of development and possible advantages and experienced problems of the selective, novel ion exchange membrane processes.

8. Perspective and conclusions

From this survey, ion exchange membrane technologies clearly appear to be versatile and capable of solving quite different problems. The author feels that most of the future developments in the area will come from those developers or users that will look at these technologies as tools to cope with their specific treatment requirements. But it should be emphasized that, for any purpose, preparation of ion exchange membranes or materials is the most crucial.

In the last decade, the development of new membrane materials has gained the advantage of an interdisciplinary approach integrating recent advances in the field of material science. A number of examples developed on ion exchange membrane preparation in this paper demonstrate the interest of using innovative methods for material processing. The sol-gel process is certainly the most appropriate way to produce purely inorganic or hybrid ion exchange membranes with various reactivity or permselectivity, and phase inversion is the key steps for organic ion exchange membrane. But what should be emphasized here, as a result of these intensified research efforts, much has been accomplished in the past decade, and we are finding the potential applications for a given membrane. As shown in Fig. 24, conventional mode starts from a specific application. To satisfy with a specific requirement, one had to choose a “proper” mem-

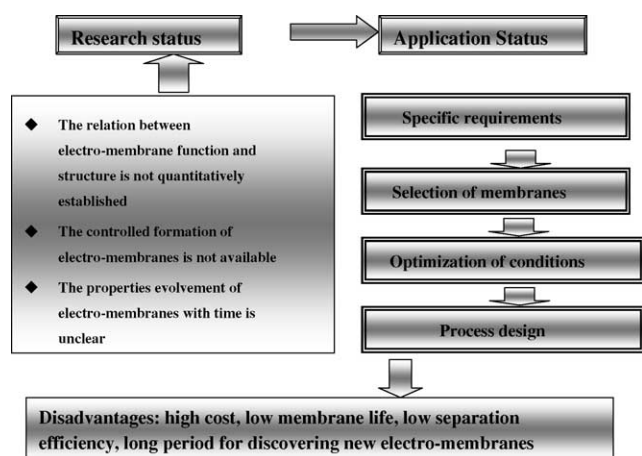


Fig. 24. Current status in research and application of electro-membrane fields.

brane from the “sea of membranes”, optimize the operational condition and then design the process. Such application status is limited by the current researches status; the relation between electro-membrane function and structure, the controlled formation of electro-membranes and the properties evolution of electro-membranes with time leave to be quantitatively determined at this time. Obviously, in the future, it is necessary to discard this old mode and establish a new one for synthesis and application of ion exchange membranes. As shown in Fig. 25, the new mode is expected to go the reverse route to the conventional one: designing a specific membrane for a specific purpose. The new mode starts from the needed membrane properties for a specific process, determination of membrane properties, membrane structure and finally designs the membrane from molecular level, i.e., such

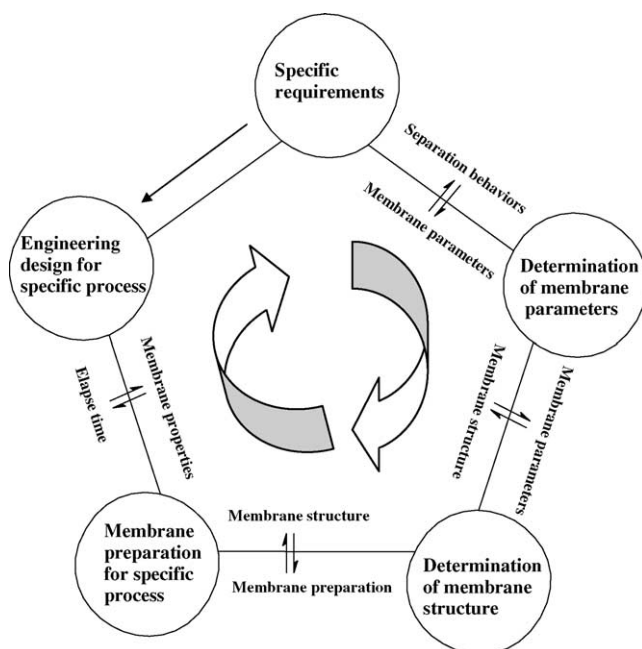


Fig. 25. New mode for an electro-membrane designed for a specific process.

mode goes from molecule to process. At this time, there is no need to choose one membrane from a lot of membranes for a specified process and thus time and money are saved. But to truthfully realize this aim, at least the following jobs should deserve much attention.

- The relation between the separation results and the needed membrane function should be underlined.
- The relation between electro-membrane function and microstructure should be quantitatively established.
- The relation between the microstructure and formation parameters of electro-membranes should be quantitatively determined.
- The evolution of electro-membranes properties and microstructure with elapse time should be decided.

Apart from the preparation of ion exchange membranes, the technical and commercial relevance of the ion exchange membrane-based processes should also be considered. As analyzed by Strathmann in his recent work [35], some of the applications can be considered as state-of-the-art technology, such as the applications using conventional electrodialysis, production of pure water using continuous electrodeionization and some specific applications using bipolar membranes, such as producing organic acid from the fermentation broth or recovering HF and HNO₃ from a waste stream generated by neutralization of a steel pickling bath; while other applications are still in the pilot plant or even laboratory stage, such as the production of acids and bases by electrodialysis with bipolar membranes. Often ion exchange membrane separation processes are in competition with other mass separation techniques and their application is determined by economic considerations. In some applications, ion exchange membrane processes provide higher quality products or are more environmentally friendly and will therefore be used in spite of a cost disadvantage. Also, increasing costs of raw materials and environmental awareness have increased the application of ion exchange membrane separation processes especially in highly industrialized and densely populated countries.

Actually, the development of electro-membrane system has gained the advantage of an interdisciplinary approach integrating recent advances in the every field of science and technology, and therefore, technologists and researchers should give exceptional considerations to interdisciplinary knowledge, such as material, inorganic, polymer science and technology, mathematics as well as engineering to solve some multifold problems, such as apparatus design and operating conditions optimum in electro-membrane processes.

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