1

Overview of Ion Exchange Membranes

1.1 Definition and Classifications

Ion exchange membranes (IEMs) are typically made up of a hydrophobic polymer matrix and ionic groups and can be classified into anion exchange membranes (AEMs) and cation exchange membranes (CEMs) according to the type of ionic groups grafted onto the membrane matrix. CEMs that are fixed with negatively charged groups ($-SO_3^-$, $-COO^-$, etc.) conduct cations but repel anions, while AEMs containing positively charged groups ($-NH_3^+$, $-NRH_2^+$, $-NR_2H^+$, $-NR_3^+$, PR_3^+, $-SR_2^+$, etc.), permit the permeation of anions but retard cations [1, 2]. The typical polymer architectures of IEMs are shown in Figure 1.1a, while the typical groups are shown in Figure 1.1b [3].

According to the connection of ionic groups to the polymer matrix, IEMs can also be categorized as homogeneous and heterogeneous membranes. In homogeneous membranes, the charged groups are chemically bonded to the membrane matrix, and in heterogeneous membranes, they are physically mixed with the membrane matrix [4]. There are many other classification methods, and as a summary, we provide Table 1.1, listing the main categories of IEMs [5].

1.2 Profile of IEMs

Research on IEMs has a long history, dating back to 1890 when Ostwald investigated the properties of semipermeable membranes [6]. It was found that none of the electrolytes could permeate through membranes if these membranes were impermeable to either anions or cations. To explain this phenomenon, the author postulated the "membrane potential" at the boundary between a membrane and its surrounding solution, which was derived from the difference in concentration. The existence of such a boundary was confirmed by Donnan in 1911 [7]. The concentration equilibrium that led to the so-called "Donnan exclusion potential" was described with a mathematical equation. In 1925, Michaelis and Fujita used homogeneous, weak acid collodion membranes to initiate practical basic studies relevant to IEMs [8]. In the 1930s, Sollner demonstrated the idea of a mosaic or amphoteric membrane that had both positively and negatively charged moieties that revealed
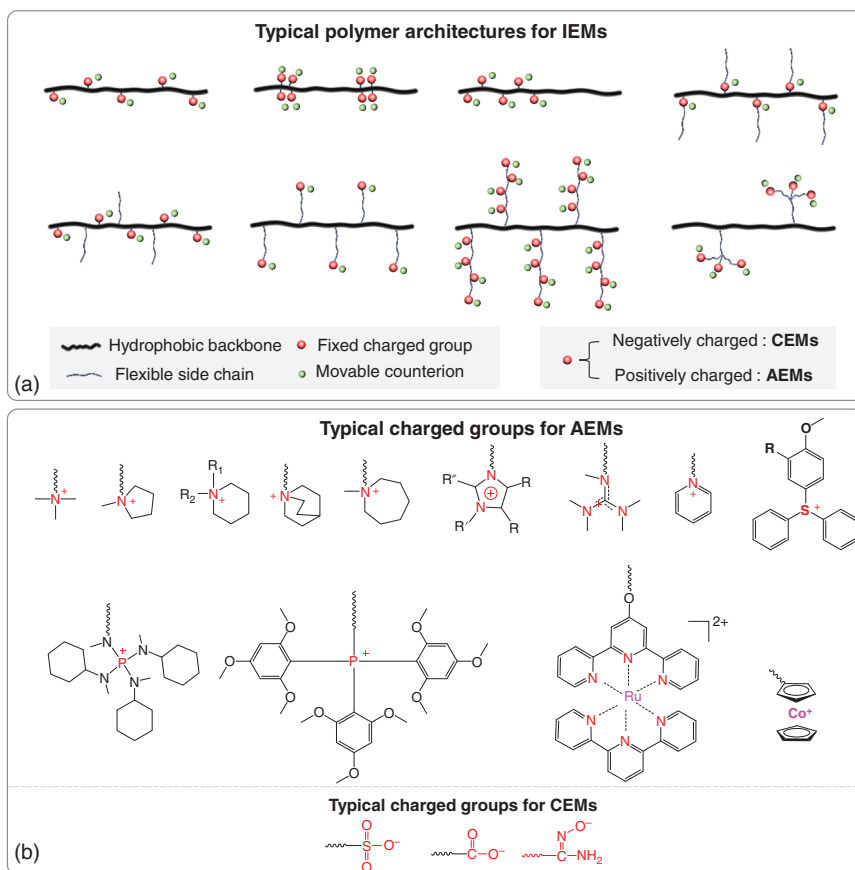
Figure 1.1 Schematic showing the structure of ion exchange membranes (IEMs). (a) Typical polymer architectures, (b) representative positively charged groups of anion exchange membranes (AEMs), while anionic groups, including sulfonate groups, carboxylate groups, and amidoxime groups, are usually introduced for cation exchange membranes (CEMs).

distinctive ion transport phenomena [9]. The increasing interest in IEMs that were used in industrial processes stimulated the development of synthetic IEMs based on phenol–formaldehyde polycondensation around 1940 [10]. Meyer and Strauss proposed an electrodialysis process that was performed in a configured cell [11]. This cell consisted of two compartments formed by an AEM and a CEM placed between two electrodes. In most practical electrodialysis processes, a stack into which multiple electrodialysis cells were arranged was used.

However, at that time, the industrial implementation of electrodialysis was still impeded by the absence of IEMs with good properties, especially low membrane resistance. This situation improved in the 1950s. Juda et al. from Ionics Incorporated [12] and Winger et al. from Rohm and Haas Company [13] promoted the development of IEMs that had improved performance in terms of chemical stability, selectivity, and electric resistance. Electrodialysis on the basis of these membranes

Table 1.1 The main categories of ion exchange membranes.

The basis of classification	Type	Description
According to the type of ionic groups	Cation exchange membrane	Selectively transport cations but repel anions
	Anion exchange membrane	Selectively transport anions but repel cations
According to the arrangement of an ionic group within the membrane	Amphoteric ion exchange membrane	Membranes contain both positively and negatively charged groups and these groups are distributed randomly in membranes
	Zwitterionic ion exchange membrane	Membranes contain an equal number of positively and negatively charged groups.
	Mosaic ion exchange membrane	Membranes are made up of a set of anion and cation exchange elements arranged in parallel
	Bipolar ion exchange membrane	A kind of composition membrane that at least is composed of a cation-selective and an anion-elective layer
	Monovalent anion perm-selective membranes	Membranes can separate monovalent ions from multivalent ions
According to the connection way of ionic groups	Homogeneous ion exchange membrane	Ionic groups are covalently connected to polymer backbone
	Heterogeneous ion exchange membrane	Ionic groups are physically mixed with polymer matrix
	Semi-homogeneous ion exchange membrane	The connections combine above two ways
According to the variety of membrane materials	Inorganic ion exchange membranes	Mainly made up of inorganic materials
	Organic ion exchange membranes	Mainly made up of organic polymer materials
	Inorganic–organic (hybrid) ion exchange membranes	Mixing inorganic materials with organic polymers at the molecular level
According to the cross-sectional structure of membrane	Symmetric ion exchange membranes	Symmetric structure of cross-section
	Asymmetric ion exchange membranes	Asymmetric structure of cross-section
	Composite ion exchange membranes	Covering asymmetric membranes with one or several layers

(Continued)

Table 1.1 (Continued)

The basis of classification	Type	Description
According to pore structure of membranes	Dense ion exchange membranes	Having almost no free volume within membranes
	Microporous ion exchange membranes	Membranes contain pores with size below 2 nm which consist of charged microporous polymers or mixed materials (polymers blended with microporous fillers, such as COFs, MOFs, and graphene)
	Porous ion exchange membranes	Membranes prepared by phase inversion process contain pores with size above 2 nm and are mainly used for diffusion dialysis or electro-nanofiltration

is recommended as an industrial process that demineralizes and concentrates electrolyte solutions. Since then, IEM-based electrodialysis has witnessed wide applications in many fields. Some important examples are listed as follows: (i) In the 1960s, Asahi Co. performed the first salt production from seawater with monovalent ion permselective membranes [14]; (ii) In 1969, electrodialysis reversal (EDR) was invented that could run stably without any precipitation and deposition on both electrodes and membranes [15]; (iii) In the 1970s, DuPont developed a series of CEMs (widely known as Nafion®) made up of sulfonated polytetrafluorethylene [16]. These CEMs are chemically stable and highly conductive, and thus have still been widely used, such as in energy storage (e.g. flow batteries) or conversion systems (e.g. fuel cells); (iv) In 1976, Chlanda et al. presented a new concept of a bipolar membrane that consisted of an AEM layer and a CEM [17], and this concept is still widely studied [18, 19].

Nafion® series combining both excellent electrochemical and physical properties is widely used but hampered by high manufacturing costs. Therefore, alternatives to low-cost hydrocarbon-based polymers have received much attention since around 2000, such as poly(phenylene oxide) (PPO), polyimide (PI), poly(ether sulfone) (PES), poly(ether ketone) (PEK), and polystyrene (PS) [20]. During the membrane-formation process, the charged moieties can self-assemble into a hydrophilic phase within the hydrophobic matrix, and thus, these membranes are called microphase-separated IEMs. This microstructure is crucial to IEM performance in terms of ion conductivity, ion selectivity, mechanical stability, etc. [20–25]. Molecular engineering strategies to enhance polymer self-assembly into highly ordered microstructures are required for high-performance IEMs. Over the past two decades of development, optimal self-assembly has been realized mainly via the

following strategies [3]: (i) Densely grafting charged groups to increase the local size of the hydrophilic region (i.e. densely charged or block-type IEMs), (ii) enhancing the mobility of charged segments by introducing flexible spacers between charged groups and the backbone (i.e. side-chain-type IEMs), (iii) introducing secondary interactions such as hydrogen bonding, cation–dipole interactions, and π–π stacking as supplemental driving forces, (iv) introducing the fluorine element with both superhydrophobicity for enhanced contrast of hydrophobic and hydrophilic phases and a strong electron-withdrawing effect for improved dissociation degree of sulfonate moieties, and (v) crystallizing the polymer backbone as robust hydrophobic phase and arranging the charged groups into the continuous ion channels.

Studies on microphase-separated IEMs focus on optimizing the micromorphology from the perspective of enhancing the self-assembly of ionic groups [24]; however, there are very few examples that can precisely form the microstructure at the nanoscale [26]. In addition to the hydrophilic phase acting as ion-conducting channels, micropores are also employed for ion conduction. Constructing micropores within membranes can be achieved via covalent organic frameworks (COFs). For example, in 2018, Kong et al. fabricated positively charged COF membranes through molecular precursor engineering and observed a remarkable hydroxide ion conductivity of over 200 mS/cm [27]. We employed an interfacial growth strategy to successfully construct COF membranes that contained ordered channels with a size of approximately 1.4 nm in size and a large number of hydrogen bonding sites [28]. These membranes enabled very high selectivity of monovalent ions over divalent ions, for example, a selectivity of approximately 217 for Li^+/Mg^{2+}. However, most crystalline COFs suffer from poor processability and low mechanical flexibility [29], which may hinder their widespread use in making large-scale IEMs.

Polymer materials do not have this problem, and the construction of polymers of intrinsic microporosity (PIMs) for microporous membranes has been of great interest. In contrast to polymers for microphase-separated IEMs, PIMs (first developed by Neil B. McKeown et al. in 2004 [30]) usually consist of polymer backbones that are much more rigid and contorted, and the inefficient packing of these backbones can create sufficient intermolecular voids (i.e. micropores) [31–34]. In 2016, our group first observed the fast hydroxide ion transport within membranes from quaternized Tröger's base (TB) polymers. This result stimulated many other studies related to positively charged PIMs, including cross-linked quaternized TB polymers, trimethyl benzyl ammonium-grafted ladder polymers [35], and copolymers of poly(spirobiindane-aryl ether sulfone) with quaternized side chains [36]. Negatively charged PIMs are also employed to construct IEMs. For example, Tan et al. reported a series of amidoxime-based PIMs synthesized from the post-modification of dibenzodioxin-based ladder polymers [37]. Membranes of these polymers are effective in selective ion conduction in alkaline aqueous solutions. However, they may become much less conductive in neutral media, as amidoxime groups are ionizable only in aqueous solutions with pH values exceeding 13. Sulfonated PIMs can avoid this problem, and the current materials developed are synthesized through the post-sulfonation of polyxanthene [38] and

ladder polymers based on spirobifluorene [39]. As ion transfer in PIM-based IEMs occurs in micropores, control over pore chemistry and pore architecture is at the center of related research.

Apart from organic polymeric materials, inorganic materials, including zeolites, bentonite, and phosphate salts, can also be exploited to construct IEMs [40–42]. These materials can withstand higher temperatures but are subjected to high costs, relatively poor electrochemical properties, and poor mechanical flexibility [43]. To combine the advantages of both inorganic and organic materials, hybrid IEMs were developed in the late 1990s. They were fabricated by a sol–gel approach that could incorporate inorganic components (e.g. silica) into polymer membranes. These developed membranes were usually applied in severe conditions, such as higher temperatures and strongly oxidizing circumstances [43–45].

Until now, various IEMs, including inorganic–organic (hybrid) IEMs, amphoteric IEMs, mosaic IEMs, and bipolar membranes, have been available, and their position in the IEM development history is schematically shown in Figure 1.2a. With the improved properties of membrane materials in terms of selectivity, membrane resistance, thermal and chemical stability, and mechanical properties, IEM-based processes have also evolved and continuously infiltrated extensive applications (Figure 1.2b). These processes have received increasing interest in the process industries related to food, drug, biotechnology, and wastewater treatment [46–50] and in emerging technologies for coping with environmental and energy issues, such as CO_2 or water electrolyzers [51–53], aqueous organic flow batteries [54, 55], and fuel cells [56].
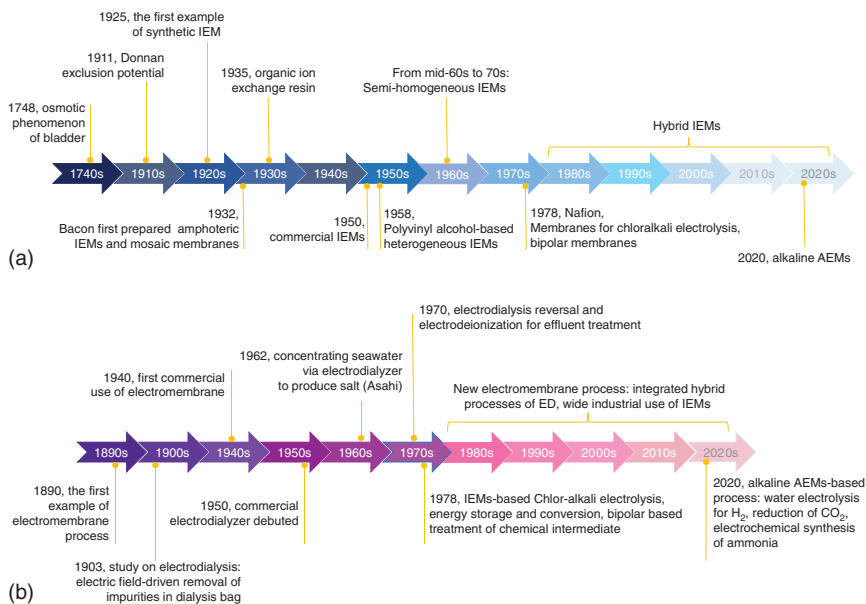

Figure 1.2 (a) The development history of IEMs and (b) IEM-based processes.

1.3   Preparation of IEMs

The synthetic approach of materials and their fabrication process for IEMs are crucial for large-scale preparation of IEMs. The synthetic approaches include the construction of a hydrophobic polymer backbone and introduction of ionic groups and are classified into three categories based on the starting materials [2, 57]: (i) post-modification approach (grafting charged groups onto polymers), (ii) bottom-up approach (direct copolymerization between monomers containing functional groups and nonfunctionalized monomers), and (iii) blend method (blending hydrophobic polymers with hydrophilic polymers with charged groups).

   Regarding the post-modification approach, a typical example is the IEM made from polystyrene and its derivatives. These polymers are synthesized starting with styrene and divinylbenzene, combining the advantages of low cost, excellent mechanical properties, and easy modification. They can be made into CEMs from post-sulfonation or AEMs from chloromethylation and subsequent quaternization, as shown in Scheme 1.1 [58–60].
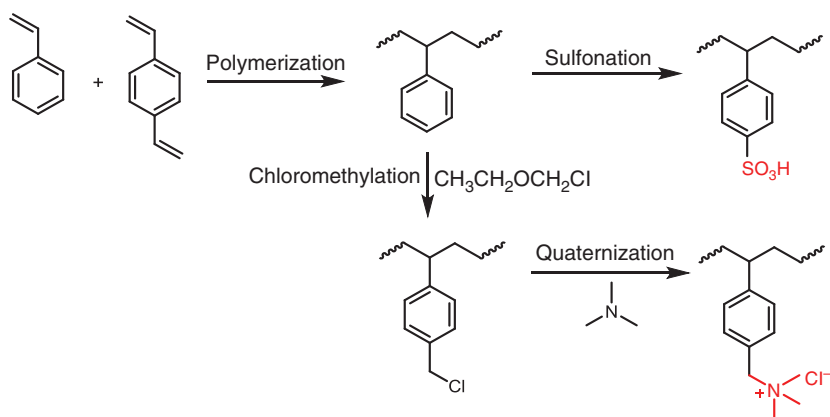
Scheme 1.1   IEMs are synthesized starting from styrene and divinylbenzene.

   The direct postmodification of existing polymers seems to be a very simple synthetic approach for IEMs. Other common polymers, such as poly(phenyl ether) (PPO) and PES, have also been used for postfunctionalization. Most of the resulting charged polymers are soluble in polar organic solvents, and thus can be processed into self-supporting films via a solution-casting method [61–69]. To improve the anti-swelling property, crosslinking is sometimes required [70–80]. For example, we triggered the crosslinking of sulfonated PPO membranes through heat treatment and observed that the resulting membranes were insoluble and maintained a high tensile strength of 52.8 MPa [74].

   It is noteworthy that, in comparison to the synthesis of CEMs (usually post-sulfonation is used), the preparation of AEMs seems to be more complicated and costly. The process for AEM usually requires chloromethyl methyl ether
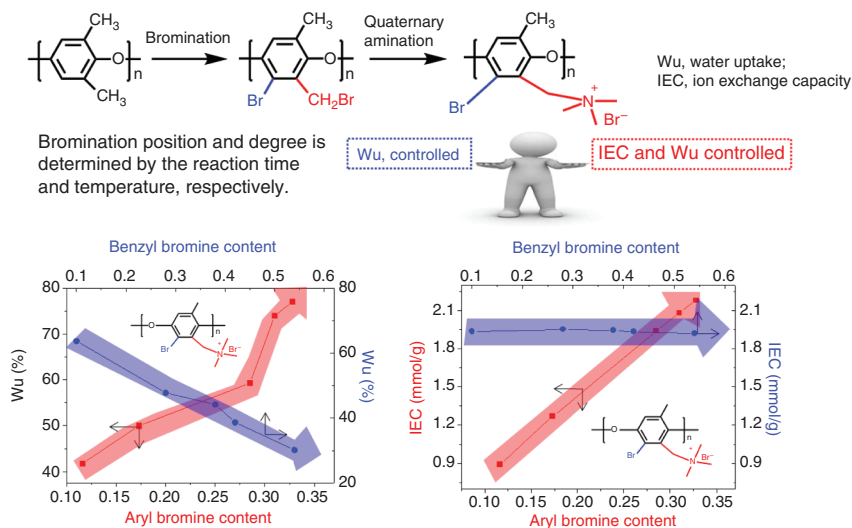
Figure 1.3 A novel synthetic route for anion exchange membrane and water uptake (WU) and evaporated ion exchange capacity (IEC) manipulating strategies based on BPPO and quaternary amination.

during the chloromethylation process, a carcinogen reagent that may cause great harm to human health [81]. Considering the economy and practice, as well as the diversity in membrane formation, direct halogenation of methyl groups that are linked to the benzene ring, instead of direct chloromethylation of the benzene ring, is a better choice due to the cancelation of the use of chloromethyl methyl ether. For example, a simple and practical method for the preparation of AEMs is shown in Figure 1.3. This preparation included the bromination of PPO and subsequent quaternization. Control over the reaction position (benzyl substitution or aryl substitution) and content of bromination, as well as the amination-crosslinking processes, are key to the properties of the resulting membranes [82, 83]. Based on this approach, a series of IEMs have been commercially manufactured and have been widely used in diffusional dialysis to recover inorganic acid under different conditions [84–86], electrodialysis [87], nanofiltration, ultrafiltration [88, 89], fuel cells [90], and in the separation of different anions [91, 92].

Another widely used approach that can avoid the chloromethylation process is to synthesize polymers starting from monomers containing halogenated hydrocarbons (e.g. vinylbenzyl chloride [93–95]). These polymers can be made into AEMs via a simple amination reaction (Scheme 1.2a). Terephthaloyl chloride could be formed into poly(p-phenylene dichloroethene) with a π-conjugated system and benzyl chloride groups via the McMurry coupling reaction, and the resulting polymers could be converted into positively charged polymers through quaternization (Scheme 1.2b) [96]. Notably, piperidone and its derivatives as raw materials have recently gained great attention in making poly(arylene piperidinium) AEMs due to their outstanding alkaline stability [97, 98]. These membranes are synthesized from the super acid-catalyzed polycondensation followed by quaternization (Scheme 1.2c),
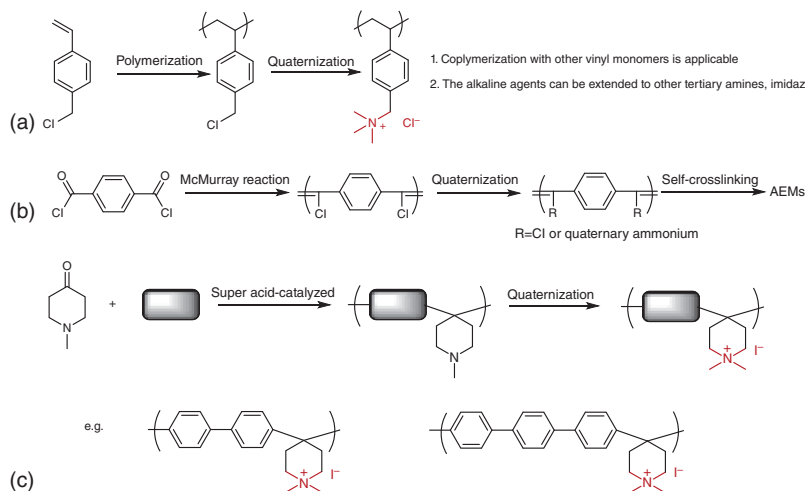
Scheme 1.2 Typical examples of the synthesis of AEMs starting from uncharged functional monomers.

and are now mainly used for AEM fuel cells. Their use in wide applications is highly expected.

For bottom-up synthesis, the copolymerization of commercially available monomers with charged groups and hydrophobic monomers seems to be a simple method. In 2004, Xing et al. reported a series of sulfonated PEK copolymers that were synthesized via aromatic nucleophilic polycondensation of 5,5′-carbonylbis (2-fluorobenzenesulfonate) (a charged monomer) with hexafluoroisopropyli-dene diphenol and 4,4′-difluorobenzophenone [99]. The major advantage of this approach over post-modification is the precise control over ion exchange capacity by tuning the molar ratio of reactant monomers. The resulting polymers could be processed into robust membranes from a solution-casting approach. To diversify the IEMs from bottom-up synthesis, many other polymerization processes have been employed, such as cyclo-polycondensations of dipiperidines and tetrakis(bromomethyl)benzene for N-spirocyclic quaternary ammonium ionomers [100], and acid-catalyzed polyacylation of pre-quaternized diarene monomers and dibenzoic acid monomers for PEK containing charged side chains [101, 102].

In the above solvent-aided polymerization, solvents were required to obtain the polymer solution, but may bring toxicity risks to the environment. To address this issue, a solvent-free approach via in situ polymerization has been developed [70, 103–105]. The strategy replaced the organic solvents with liquid monomers that were fully incorporated into the resulting membranes. As illustrated in Figure 1.4, brominated PPO was first dissolved in a liquid monomer mixture of vinylbenzyl chloride and styrene, instead of common organic solvents, to perform both crosslinking and quaternization, thus yielding imidazolium-based AEMs [106].

Pore soaking or filling is another approach to introduce charged segments into the pores of polymer films, producing IEMs. Porous films are usually commercially available, cost-effective, and insoluble in common solvents, such as
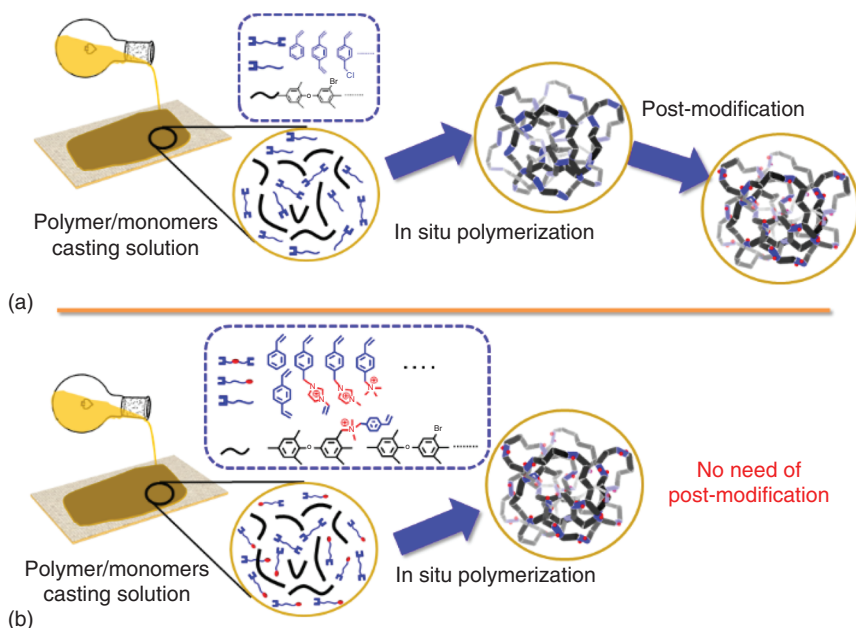
Figure 1.4 Schematic illustrations of (a) conventional, (b) upgraded in situ polymerization strategies for the preparation of IEMs.

films of hydrocarbon or fluorocarbon polymers (polytetrafluoroethylene (PTFE); fluorinated ethylene propylene (FEP), perfluoroalkoxy alkanes (PFA), ethylene tetrafluoroethylene (ETFE), poly (vinylidene fluoride) (PVDF)). Membranes made from this method exhibit excellent mechanical properties and show an advantage in manufacturing cost. For example, Young Moo Lee et al. successfully filled the pores of porous polyethylene (PE) substrates with poly(aryl-*co*-aryl piperidinium), and the reinforced membranes could be applied in alkaline membrane fuel cells [107, 108].

Although various synthetic approaches to IMEs have been developed, not all of the preparations have led to commercialization. There are many obstacles along the way from laboratory synthesis to large-scale production. As a summary of this section, Table 1.2 lists the main commercial IEMs and their main properties.

1.4 Applications

Based on advanced membrane fabrication technologies and rational material design, IEMs with a good combination of low electrical resistance, high chemical and thermal stability, excellent mechanical properties, and high ion selectivity have been developed. The rapid development of materials for IEMs promotes the evolution of traditional IEM-related processes, such as diffusion dialysis, reverser electrodialysis, membrane capacitive deionization, and bipolar membrane electro-dialysis. These processes can dispose of wastewater in a wide range of new industrial

Table 1.2 The properties of commercial IEMs from famous membrane companies.

Company	Name	Type	Thickness (mm)	IEC[a] (mmol/g)	R_m [b] (Ω cm^2)	Preparation
FuMA-Tech GmbH, Germany	fumasep® FKB	CEM[c]	0.10–0.13	1.2–1.3	4–6	Polymer dissolution and casting
	fumasep® FAB	AEM[d]	0.10–0.13	1.0–1.1	4–7	
ASTOM Co., Japan	NEOSEPTA® CMX	CEM	0.17	—	3.0	Monomer polymerization
	NEOSEPTA® AMX	AEM	0.14	—	2.4	
Asahi Glass Co., Ltd., Japan	Selemion® CMV	CEM	0.13–0.15	—	2.0–3.5	Desalination
	Selemion® ASV	AEM	0.11–0.15	—	2.3–3.5	Desalination
Chemjoy Co., Ltd., China	Chemjoy® CJMCED	CEM	0.14–0.16	0.9–1.5	<2	In situ polymerization
	Chemjoy® CJMAED	AEM	0.14–0.16	0.9–1.2	<4	Desalination
Tianwei Co., Ltd., China	TWEDC	CEM	0.10–0.13	—	<4	Pore filling
	TWEDA	AEM	0.13–0.16	—	<4	Pore filling
	TWDD	BPM	0.18–0.23	—	–	BPPO matrix
Tingrun Co., Ltd., China	JCM-II	CEM	0.16–0.23	1.8–2.9	1–7	Pore soaking
	JAM-II	AEM	0.16–0.23	1.6–2.2	4–10	Pore soaking

a) IEC: ion exchange capacity.
b) R_m: membrane area resistance (0.5 mol/l NaCl, 25 °C).
c) CEM: cation exchange membrane.
d) AEM: anion exchange membrane.

applications, including salt concentration, cleaner bioproduct production, and salt resource valorization. Notably, many emerging IEM-based technologies have been widely employed to address the issues related to the environment and energy, including fuel cells that convert chemical energy to electric energy, flow batteries that store energy on a large scale, and solar-driven water splitting that produces H_2 and O_2. The detailed applications can be found in the subsequent chapters.

1.5 Potentials

IEMs have broad application prospects in the treatment of high-salinity wastewater to meet the environmental requirement of zero discharge. For example, the

transformation processes of coal, such as gasification, liquefaction, and synthesis gas preparation, produce large amounts of high-salinity wastewater that contain toxic and harmful substances, such as phenols, cyanides, oils, and ammonia nitrogen. Wastewater treatment has largely hindered the development of the coal chemical industry. Currently, complex treatment processes, including pretreatment, biochemical treatment, ultrafiltration, reverse osmosis, salt concentration, and evaporation crystallization, still face great challenges of concentrated brine discharge, high investment in evaporation equipment, high operating costs, and low utilization of regenerated salt resources. In contrast, IEM-based electrodialysis technology can concentrate saltwater more economically and effectively, with a high concentration of the resulting NaCl solution that increases to 200,000 mg/l. Therefore, this technology meets the concentration requirements for salt production and offers a new solution for the treatment of coal chemical wastewater, as well as the comprehensive utilization of salt resources. With the increasing improvement of national environmental emission standards and the recognition of national environmental value (i.e. lucid waters and lush mountains are invaluable assets), IEM-based technologies will find their increasingly important role in the reduction and resource recovery of high-salinity wastewater and will transform the industrial production modes of the coal chemical industry, metallurgy, printing and dyeing, and paper-making in terms of reducing both the cost and emissions of carbon dioxide and solid waste.

The future development of IEMs should closely surround the vision of "carbon peaking and carbon neutrality." High-performing IEMs in terms of high ion conductivity, excellent chemical and mechanical stability, low manufacturing cost, and easy production on a large scale are required to promote the evolution of IEM-based technologies that cope with carbon emission issues and steadily improve the conversion efficiency of mass transfer and energy conversion in the chemical industry. These technologies include bipolar membrane electrodialysis for acid/alkali production, CO_2 or water electrolyzers that produce resources, H_2/O_2 or ammonia/O_2 fuel cells that convert chemical energy into electric energy, organic flow batteries that store energy on a large scale, and osmotic energy-conversion devices that are based on the salinity gradient. IEM-based technologies are also receiving attention in ion separation, such as mono-/divalent ion separation, Li^6/Li^7 separation, and F^-/Cl^- separation. Notably, successful membranes may differ greatly in the emphasis placed on certain aspects of their applications. For example, chemical stability is extremely important for AEMs used in alkaline fuel cells, while ion selectivity should be considered first for preparing monovalent anion permselective membranes.

It can be forecasted that an increasing number of advanced membrane materials will be developed and will constantly transform existing membrane-based technologies. The formulation of their industrial standards should be considered urgently. Along with the development of IEM materials, researchers also need to consider IEM application processes and achieve a tailored fit for IEMs. Chemical engineering issues occurring in the related processes should also be given much attention. The following aspects are suggested to be considered for the IEM community:

(1) With the assistance of computer simulation, developing structurally biomimetic membrane stack gaskets helps to optimize the distribution of feed fluids in the

membrane stack and achieve the uniform distribution of fluid streamlines in the chamber, thus effectively reducing fluid flow resistance, pressure drop, and pump loss.

(2) Advanced manufacturing technologies, such as 3D printing, photocuring molding, plasma etching, and micronano processing, are employed to manufacture "framework-style" mesh grids that contribute to regulating fluid disturbances and reducing the thickness of the membrane–solution interface layer. In some specific application scenarios, such mesh grids may also help to reduce mass transfer resistance and improve the limited current density.

(3) Based on micro/nano processing platforms, microfluidic membrane chip technology that combines a chip, membrane materials, and catalytic materials, is developed to realize synergistic coupling between mass conversion and energy conversion.

(4) On the basis of quantum chemical calculations and machine learning techniques, develop advanced intelligent membrane devices that integrate intelligent synthesis, in situ characterization, intelligent acquisition, and intelligent response. Building an artificial intelligence management and control system and interconnecting an intelligent synthetic cloud database will help membrane devices to match well with both the front-end feeding units and the back-end processing units, and thus realize chemical processes that are intelligent, intensive, and of low carbonization.

In short, it is important to understand and solve scientific problems, technical issues, and engineering matters occurring during the development, production, and application of IEMs. The future development of IEMs should closely surround both the industrial demand and the vision of "carbon peaking and carbon neutrality" and promote them into ones having better performance in terms of low resistance, high chemical and mechanical stability, and high ion selectivity. These membranes will transform IEM-based technologies, which can make many chemical processes more energy-efficient and environmentally friendly.

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