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## Ion exchange membranes: New developments and applications



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### ABSTRACT

Ion exchange membranes (IEMs) have great potential in diverse applications and play prominent roles in addressing energy and environment related issues. Over the past decade, the development of IEMs has attracted much research attention in terms of materials, preparation and applications, due to their academic and industrial values. In this review, the advances in diverse IEM materials are summarized, providing insights into the fundamental strategies to achieve targeted properties. Apart from the intrinsic features of materials, optimized preparation methods are crucial to improve the quality of IEMs, which are discussed in detail. New IEM materials bring new applications, which are summarized in this review. Finally, the opportunities and challenges in the chemical stability of IEM materials, controllable fabrication of IEMs, and integration applications of IEMs are identified.

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## 1. Introduction

Ion exchange membranes (IEMs) are typically composed of hydrophobic substrates, immobilized ion-functionalized groups, and movable counter-ions. Depending on the type of ionic groups, IEMs are broadly classified into cation exchange membranes (CEMs) and anion exchange membranes (AEMs). Naturally, the ion-functionalized groups attached onto the IEMs will dissociate after the penetration of sufficient water molecules, releasing cations or anions for the transfer of corresponding ions. The most commonly functional moieties in CEMs contain sulfonic acid, phosphoric acid and carboxylic acid groups [1]. Quaternary ammonium cations, imidazole cations, and guanidinium cations are generally anchored onto the polymer backbones to obtain AEMs [2].

Since last century, IEMs as a new type of material have received much research attention because of their applications in a variety of fields. IEMs are used in electrodialysis to concentrate or dilute aqueous or non-aqueous electrolyte systems, and in diffusion dialysis to recover acid or alkali from waste acid or alkali solutions [3]. Recently, IEMs have significantly contributed to overcome the problems associated with energy and environment. Diverse electrochemical technologies such as polymer electrolyte membrane fuel cells [4], redox flow batteries [5], reverse electrodialysis cells [6], and water electrolysis [7] utilize IEMs that separate and transport ions between the anode and cathode to balance the electron flow in the external circuit. Thus, there is an increasing worldwide interest in the use of IEMs to develop renewable energy sources.

Considering the importance of IEMs for contemporary developments, they have been extensively studied in academic and industrial fields. To satisfy various requirements of traditional and newly emerging IEM-related fields, research efforts have been devoted to developing novel IEMs or to modifying pristine IEMs for certain targeted activity. To date, most of the IEMs consist of polymeric backbones prepared by either post-functionalization of pre-existing polymers or direct polymerization of functionalized monomers. To convert the prepared polymers to IEMs, suitable membrane formation techniques are needed, and these techniques have been widely studied in the past. IEMs with excellent qualities can be assembled into various devices and processes. Materials, preparation methods, and final applications are all crucial in the field of IEMs.

In 2005, a review on IEMs was published in *Journal of Membrane Science* [8]. The review was extensively cited, indicating that the research enthusiasm on IEMs is ever-growing. In the current decade, great efforts have been devoted to upgrading IEMs, as illustrated by the chronology of IEM related publications over the past decade in Fig. 1. We realize a brand-new review to summarize the progresses of IEMs is given urgently. Particularly, with the rapid progress in nano-science, the regulation and control of polymer structures make for the formation of ionic channels, which is a new development in this field. Newly emerging preparation methods are worthy of research attention. Over the past

decade, most of the IEM applications are expected to solve issues related to energy and environment, and these aspects are becoming the hot topics in the present literature. Herein, the recent progress in IEMs along with the line of materials-preparation-applications will be reviewed.

## 2. Materials

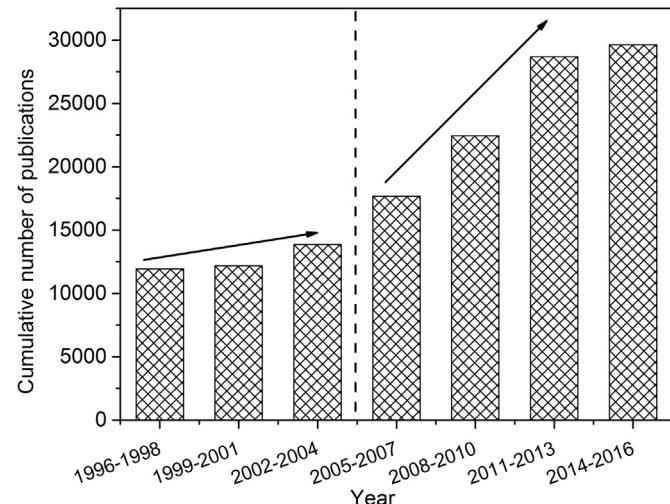
As shown above, CEMs and AEMs receive wide research attention. Besides, recently reported monovalent ion perm-selective membranes (MIPMs), mixed matrix membranes (MMMs), and bipolar membranes (BPMs) are also included in the current review.

### 2.1. Cation exchange membranes (CEMs)

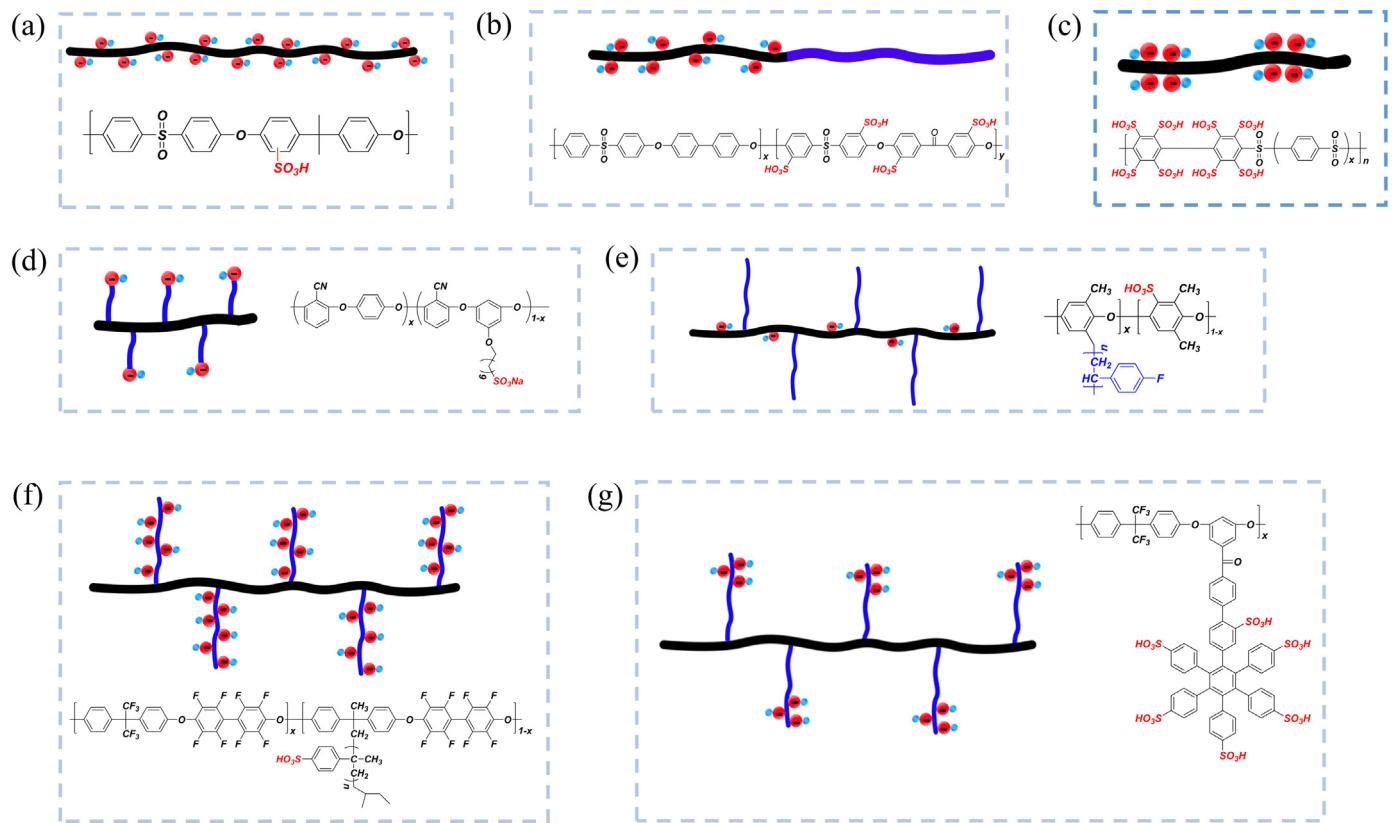
CEMs generally contain sulfonic acid groups, phosphoric acid groups, sulfonamides, and azole derivatives. Diverse polymer materials including poly(ether sulfone) (PES), poly(ether ketone) (PEK), polybenzimidazole (PBI), polyimide (PI), poly(phenylene), polyphosphazene, and polyvinylidene fluoride (PVDF) were investigated as the backbones for CEMs. Besides, the variation in the topological architectures of polymeric ionomers has been confirmed to significantly affect the overall performance of CEMs. Block CEMs, side chain type CEMs, comb-shaped CEMs and densely functionalized CEMs have been extensively reported.

#### 2.1.1. Main chain type CEMs

CEMs were initially developed from the main chain structure, in which cationic groups are directly attached onto the polymer backbones without spacers (Fig. 2a). This type of CEMs is mainly prepared by either post-sulfonation of chemically robust main



**Fig. 1.** Chronological advancement of ion exchange membrane in the past 20 years. Source: [www.scopus.com](http://www.scopus.com); Search settings: ion exchange membrane including articles, conferences, notes, books and review papers; Last accessed: August 2016.



**Fig. 2.** Polymer architecture and representative chemistry schemes of cation exchange membrane.

chains or co-polymerization of sulfonated monomers. Poly-condensation is the mostly frequently used co-polymerization reaction to obtain aromatic CEMs, which is commonly achieved through a nucleophilic mechanism. Bisphenol A is one of the most common monomers, which is employed in this type of poly-condensation, due to its high reaction activity. Apart from the nucleophilic mechanism, our groups recently explored a facile route through an electrophilic mechanism to get access to the sulfonated polymers. By polyacetylation of diarene monomers and dicarboxylic acid monomers under mild conditions, sulfonated aromatic PEK was synthesized via one-step etherification with high yield [9,10]. Besides, by supplying another 3,3',4,4'-tetraamino monomers, copolymers of PEK/PBI could be synthesized in one pot through the poly-acetylation reaction [11,12]. Although main chain type CEMs were persistently developed over the past years, the low cation conductivity is still a fatal shortcoming in restricting their potential practical applications..

### 2.1.2. CEMs based on block co-polymers

One of the most effective ways to enhance the cation conductivity of CEMs is to construct inter-connected cation conducting channels within the membrane matrix. The hydrophilic/hydrophobic discrimination between the functionalized segments and un-functionalized segments leads to phase separation on nano-scale. Aiming to facilitate the formation of well-defined nano-phase separation, one of the most efficient strategies is to explore polymers with various topological structures. By employing block copolymers (Fig. 2b) having one particular segment functionalized by dense sulfonic acid groups, excellent nano-phase separation could be achieved as observed by atomic force microscope (AFM), transmission electron microscope (TEM) or small angle X-ray scattering (SAXS).

Block polymeric CEMs can be divided into two categories: (1) typical block polymers are composed of two or three segments

having different compositions; (2) a few hydrophilic and hydrophobic segments arrange alternatively to construct a multi-block polymer. The former could be prepared via atom transfer radical polymerization (ATRP) of styrene initiated by a macro-initiator [13]. The polystyrene (PS) can be easily sulfonated with chlorine sulfonic acid. ATRP of sodium p-styrenesulfonate [14] or n-propyl-p-styrenesulfonate has also been reported in literature [15]. The latter could be synthesized via nucleophilic poly-condensation of di-phenol and di-halide oligomers. One of the oligomers can be densely grafted with sulfonic acid groups either by post-sulfonation [16,17] or by employing sulfonated monomers [18,19]. Watanabe and co-workers firstly accomplished the preparation of multi-block sulfonation co-polymers [20]. The resultant CEMs displayed surprisingly high proton conductivity, which is ascribed to well-defined ionic channels formed by the aggregated ionic clusters.

It is widely accepted that the typical block copolymer is achieved by controllable radical polymerization of aliphatic monomers. However, recent reports have suggested that the synthesis of the first type block copolymer can also be achieved by controllable poly-condensation of aromatic monomers. Ni-mediated coupling polymerization of di-chloro sulfonated monomers and oligomer was employed to obtain fully aromatic block CEMs [21]. Guiver and co-workers firstly reported fully aromatic ABA tri-block copolymers by exploiting the mono-phenoxide-terminated poly(phenyl oxide) (PPO) oligomer, which was end-capped onto the poly(arylene ether sulfone) (PAES) [22]. Excellent nano-phase separation and comparable conductivity to Nafion® was observed.

### 2.1.3. Densely functionalized CEMs

Another effective method to promote micro-phase separation is to introduce various monomers having densely aggregated cationic groups into the polymer backbones (Fig. 2c). Jannasch and co-workers reported densely functionalized CEMs by converting

fluorine atoms of perfluoro-biphenyl into sulfonic acid groups. However, the authors suggested that conductivity of the hyper-sulfonated polymers was limited by incomplete proton dissociation due to extremely highly local sulfonic acid concentration [23].

#### 2.1.4. Side chain type CEMs

Inspired by the structure of Nafion® membrane, a sequence of side chain type CEMs was prepared to improve the mobility of sulfonic acid groups, which are vital for constructing well-defined phase separation micro-morphology (Fig. 2d). The conventional method of introducing side chains on the polymer main chain is by reacting the phenol groups with 1,3-propanesultone, 1,4-butane sultone, or sodium 6-bromohexylsulfonate [24–27]. Other strategies of introducing pendant sulfonic acid groups such as azide-alkyne click reactions [28] and potassium carbonate-mediated nucleophilic substitution reactions [29] have also been developed.

Our group reported the polymerization of side chain type pre-sulfonated monomers through the poly-acylation route [12]. The ion exchange capacity (IEC) of the resulting CEMs could precisely be controlled by varying the molar ratio of sulfonated monomers in the reactants. In addition, various monomers bearing long side chains terminated with phenyl ring were synthesized for CEMs, either by pre-sulfonation or by post-sulfonation of the resulting polymers [30–32].

CEMs grafted with hydrophobic side chains separated from the sulfonic acid groups have also been reported to exhibit desired nano-phase separation morphology (Fig. 2e) [33,34]. The unique polymer architecture with hydrophilic backbone and hydrophobic side chains is responsible for the formation of well-defined ion conducting channels.

An increase in the number of functional groups is considered to be an effective way to enhance the micro-phase separation level (Fig. 2f). Okamoto's research group reported the Ni-catalyzed copolymerization of di-chloro monomers containing densely sulfonated aromatic side chains. A more well-defined nano-phase separation structure was observed compared with the CEMs produced by the monomers anchored with mono-sulfonic acid groups [35]. Further increase in the length of side chains and number of sulfonic acid groups results in comb-shaped CEMs, which possess excellent nano-phase separation and good anion conductivity (Fig. 2g). Comb-shaped CEMs could be synthesized from a few special monomers which bear alkene groups or bi-phenol terminal units for subsequent growth of side chains [36]. Polymer main chains bearing reactive C-Cl or C-Br bonds, may serve as macro-initiators for the ATRP "graft-from" reaction to get access to the comb-shaped architecture [37,38]. The "Grafting onto" reaction by linking functional side chains with a main chain via a fast kinetic has also been developed as an efficient strategy to synthesize comb-shaped CEMs [39,40].

#### 2.1.5. Cross-linked CEMs

Adequate mechanical and dimensional stability are required for CEMs. Cross-linking is an optimal strategy in improving these properties. Cross-linking a CEM can be easily achieved by heating. Sulfonic acid groups may exhibit a condensation reaction with the activated hydrogen atoms of aromatic rings at high temperatures over 100 °C [41]. Moreover, the acid-base cross-linking of sulfonic acid groups with either of benzimidazole rings [42], imidazole rings [43], pyridinium rings [44] or phthalazone groups [45] may also help to improve the mechanical property and dimensional stability of CEMs.

Alkynyl groups were introduced as terminal groups of CEM's main chains. After heating at 250 °C, the alkynyl groups derived from three main chains reacted with each other to form a stable cross-linked network [47]. Following this reaction, Lee and co-workers prepared CEMs with a 3D cross-linked network, leading

to unusual morphological transformation observed in TEM images and TEM- selected area diffraction (SAD) patterns (Fig. 3) [46]. Ionic clusters aggregated during this transformation process and perforative ionic channels were obtained. The click reaction has also been developed as a viable method to cross-link CEMs. Both the thiol-ene and azide-alkyne click reaction were demonstrated to be successful in gaining cross-linked structure under mild conditions [48,49].

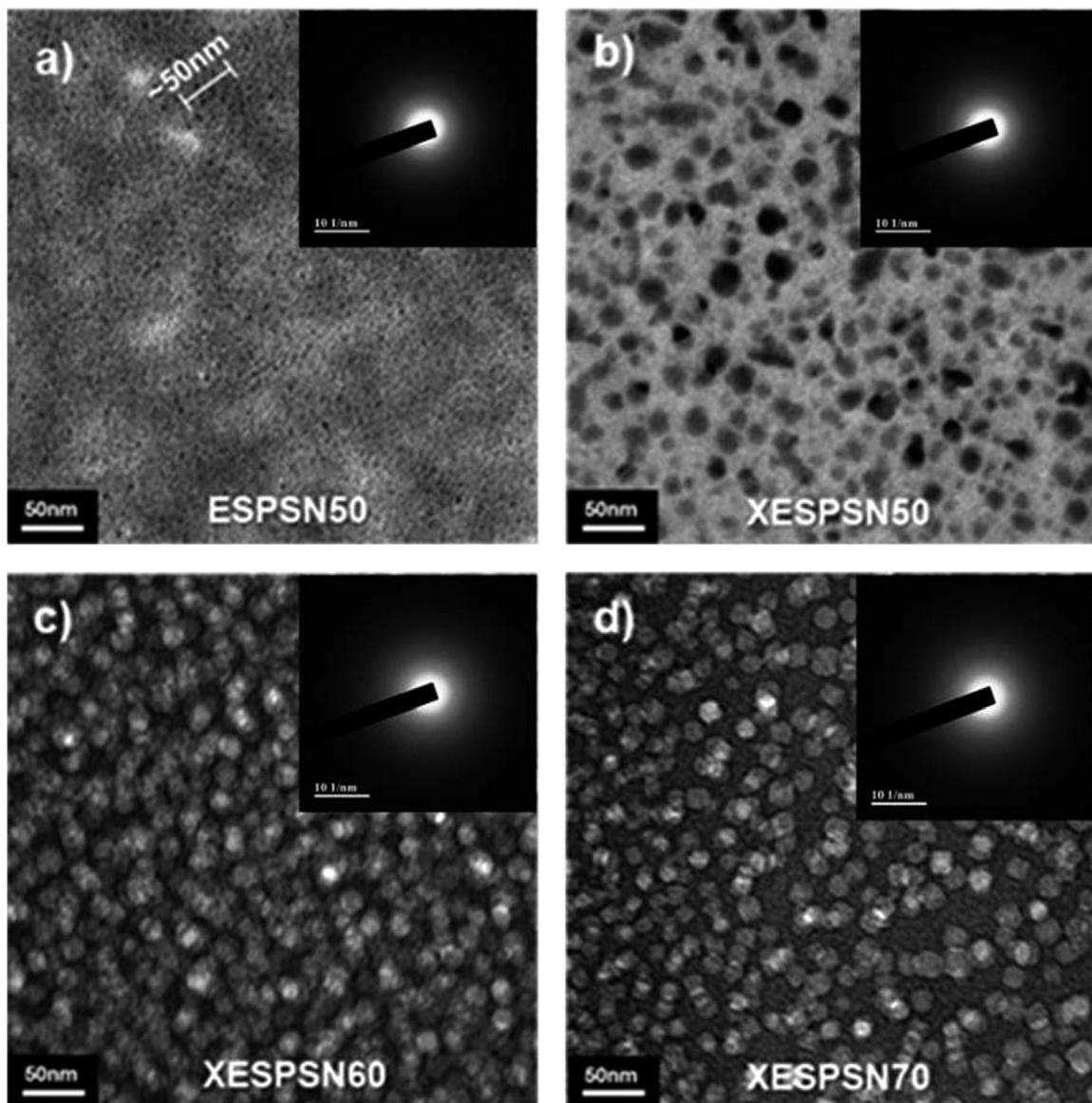
### 2.2. Anion exchange membranes (AEMs)

AEMs are generally prepared from positively charged poly-electrolytes and are designed to conduct anions while being impermeable to neutral molecules or cations. The major concerns of AEMs lie in anion conductivity, chemical stability and dimensional stability. To date, substantial research efforts have been devoted to this field, which can be classified into two main categories. The first category involves synthesis of new anion conducting groups (ACGs), while the second category involves design of a particular polymer architecture.

#### 2.2.1. AEMs with new cationic head groups

Quaternized ammonium (QA) groups (Fig. 4a) are the conventional ACGs for AEMs because of their facile synthesis procedure by simply treating a polymer precursor bearing benzyl halide groups and trimethylamine (TMA) [50–54]. However, the drawbacks of low anion conductivity and inadequate tolerance to highly alkaline environments have been blocking the AEMs' development and commercialization. In order to solve these problems, various tertiary amines with different chemical structures were investigated as precursors for ACGs. Some of these included 1,4-diazabicyclo[2.2.2]octane (DABCO) (Fig. 4b) [55], hexamethylene-tetramine (Fig. 4c) [56], N,N,N,N-tetramethyl-1,6-diaminohexane (Fig. 4d) (TMHDA) [57], and N,N,N,N-tetramethyl-1,2-diaminoethylene etc. [58]. Interestingly, some of these functional reagents (such as TMHDA, and DABCO) contain two tertiary amine groups and thus can be utilized as cross-linking reagents to prepare AEMs with improved mechanical properties and dimensional stability [59–62].

Nitrogen containing conjugated molecules are potential ACGs for AEMs. Guanidinium cations (Fig. 4e) were firstly investigated as ACGs for AEMs by Zhang and co-works [63]. Novel AEMs were easily prepared by functionalizing chloromethylated PAES with 1,1,2,3,3-pentamethyl guanidine. High basicity of pentamethylguanidine with a conjugated structure was considered to be responsible for the high anion conductivity and alkaline tolerance of this type of AEMs. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (Fig. 4f) is a kind of organic super bases which possesses a high pKa value in the order of 12. DBU based AEMs were prepared via the reaction between brominated poly(2, 6-dimethyl-1, 4-phenylene oxide) (BPPO) and DBU under mild conditions [64]. More recently, extensive research efforts have been devoted to the development of imidazolium based AEMs (Fig. 4g) [65–71] because of their easy synthesis procedure and versatile structures. It should be noted that substituents on the imidazole ring have a profound impact on the alkaline stability of imidazolium based AEMs. C2-unsubstituted imidazolium has proved to be unstable and undergoes ring opening degradation in strongly basic environments [72–76]. Afterwards, Price and co-works [77] investigated the effect of different C2 substituents on the chemical stability of imidazolium cations. Surprisingly, imidazolium with C2 position substituted by some bulky substituents (such as, tert-butyl and phenyl group) exhibits much inferior alkaline tolerance, verifying that steric hindrance protection is a less effective factor for stabilizing of the imidazolium cations. However, the authors think that acidity of the methyl protons at C2 position, which can provide alternative



**Fig. 3.** The TEM images and TEM-SAD patterns of alkynyl groups cross-linked CEMs (adapted from ref. [46]).

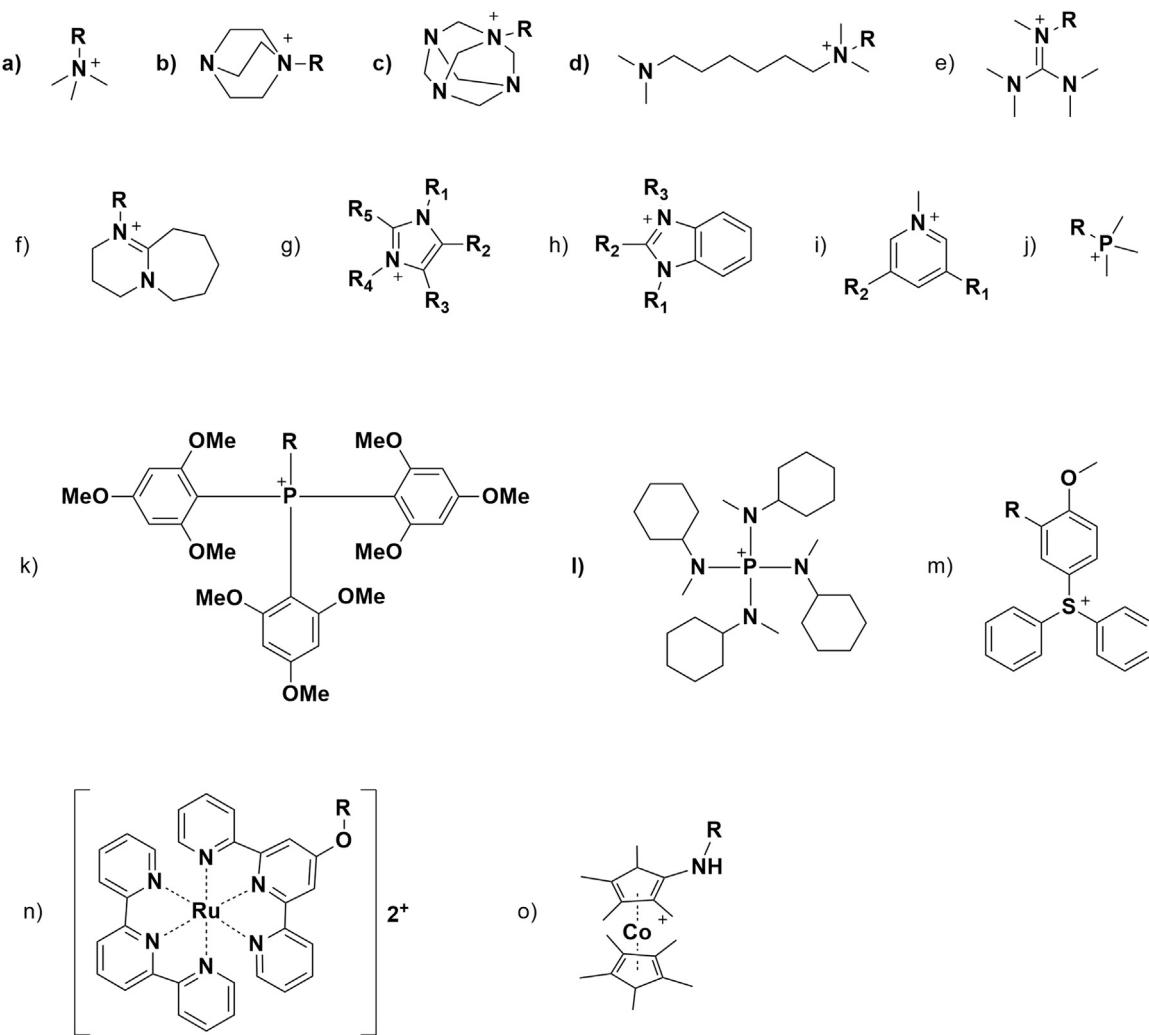
and reversible deprotonation reactions, is the key factor that decides the stability of imidazolium cations. On the other hand, Yan and co-workers [78] reported that both steric hindrance and electro-donation effects have significant influences on the alkaline tolerance of imidazolium based AEMs. To support this, the imidazolium cation with 2,4,6-trimethoxyphenyl as C2 substituent was prepared and its chemical stability was compared with C2 unsubstituted one. As expected, this type of AEMs prepared from BPPO and trimethyl-2-(2,4,6-trimethoxyphenyl) imidazole exhibited both high anion conductivity and improved alkaline stability.

Benzimidazolium cations (Fig. 4h) hold great promise to serve as ACGs for AEMs. Holdcroft and co-workers synthesized benzimidazolium based AEMs by methylation of PBI [79]. By introducing a bulky trimethylphenyl ring to the C2 position of benzimidazole, stable main chain functionalized type AEMs were successfully synthesized [80,81]. It is noteworthy that the introduction of adjacent bulky groups increases the steric hindrance around the reactive C2 position, would hinder nucleophilic attack by hydroxide ions, thus improving the stability of PBI based AEMs. Benzimidazolium based AEMs have shown advantages in

dimensional, mechanical and thermal stabilities, while simultaneously exhibiting higher anion conductivity compared with the analogous AEMs bearing quaternary ammonium and imidazolium cations [82].

Pyridine-based AEMs (Fig. 4i) were synthesized by our group and employed in the separation of various anions [83]. Improved hydrophilicity and anion permeability were observed for pyridine-based AEMs compared with the conventional QA based AEMs. Besides, the membrane also exhibited good perm-selectivity for different anions.

Phosphonium cations are recognized as promising candidates for ACGs. AEMs based on phosphonium cations can be easily prepared by reacting polymer precursors containing benzyl halide with either trimethylphosphine (Fig. 4j) [84,85] or triphenylphosphine. However, this type of AEMs have proved to be unstable in alkaline media because of severe nucleophilic attack by hydroxide ions [86]. Yan and co-workers [87–90] found that by introducing three electro-donating methoxyl groups into each phenyl ring of triphenylphosphine (Fig. 4k), cation conductivity and alkaline tolerance of phosphonium based AEMs could be greatly enhanced. This can be ascribed to both steric hindrance and electro-donating



**Fig. 4.** Commonly encountered anion conducting groups for anion exchange membrane.

effects of methoxyl groups. Another type of phosphonium cation with more complicated structure was synthesized and investigated by Coates and co-workers (Fig. 4l) [91]. Despite its relatively low IEC values, this phosphonium based AEM exhibited satisfactory cation conductivity and outstanding alkaline tolerance. It is believed that steric hindrance protection to the central phosphonium cations and delocalization of positive charges to the carbon atoms are the principle reasons for their superior chemical stability.

Tertiary sulfonium cations (Fig. 4m) act as ACGs for AEMs. Yan and co-workers [89] synthesized the first base stable sulfonium-based AEM by introducing one electro-donating methoxyl group to the phenyl ring connected to sulfonium cations.

Hickner and co-workers [92,93] prepared metal-cation functionalized AEMs by copolymerization and cross-linking of dicyclopentadiene and norbornene monomers bearing a water-soluble bis(terpyridine)ruthenium(II) complex (Fig. 4n). Hydroxide conductivity of 27 mS/cm and acceptable alkaline tolerance were observed, suggesting that the metal-cation based polyelectrolytes may serve as potential candidate for AEMs. Besides, Yan and co-workers reported permethyl cobaltocenium based AEMs (Fig. 4o) [94], which have reduced positive charges on the metal center. This cobalt based AEM exhibited excellent stability.

#### 2.2.2. AEMs with new polymer architecture

Despite numerous efforts devoted to the synthesis of new

anion conducting moieties, QA moieties are still the state-of-art ACGs for AEMs. Nowadays, more and more research efforts have been devoted to the design of unique polymer architecture to achieve higher anion conductivity and better alkaline stability. The first attempt to synthesize high performance AEMs through polymer structure design was inspired by Nafion<sup>®</sup>, which exhibits high cation conductivity because of its excellent self-assembly ability to form inter-connected ion conducting channels. A series of side chain type AEMs (Fig. 5b) were synthesized, which exhibited high anion conductivity [66,95–97]. Among these works, our group reported side chain type AEMs synthesized by one-pot poly condensation of pre-quaternized monomers [98]. For this AEM, highly flexible side chains make for the formation of well-defined nano-phase separation, resulting in high anion conductivity. Adding an aliphatic spacer between QA groups and polymer main-chains may alleviate the degradation of polymer backbones in alkaline environments.

In order to enhance the mobility of side chains to facilitate the conduction of anions, our group initially synthesized AEMs with “free shuttling” side chains via the host-guest recognition of crown ether and secondary amines (Fig. 6) [99]. Bulky terminus stopper groups were introduced to prevent slipping out of side chains. This resulted in easy depositing of host-guest interactions, which leads to AEMs having free shuttling side chains. As shown in Fig. 7, the hydroxide conductivity of this membrane is more than 180 mS/cm at 90 °C, although its IEC is only 0.68 mmol/g. A sharp increase in

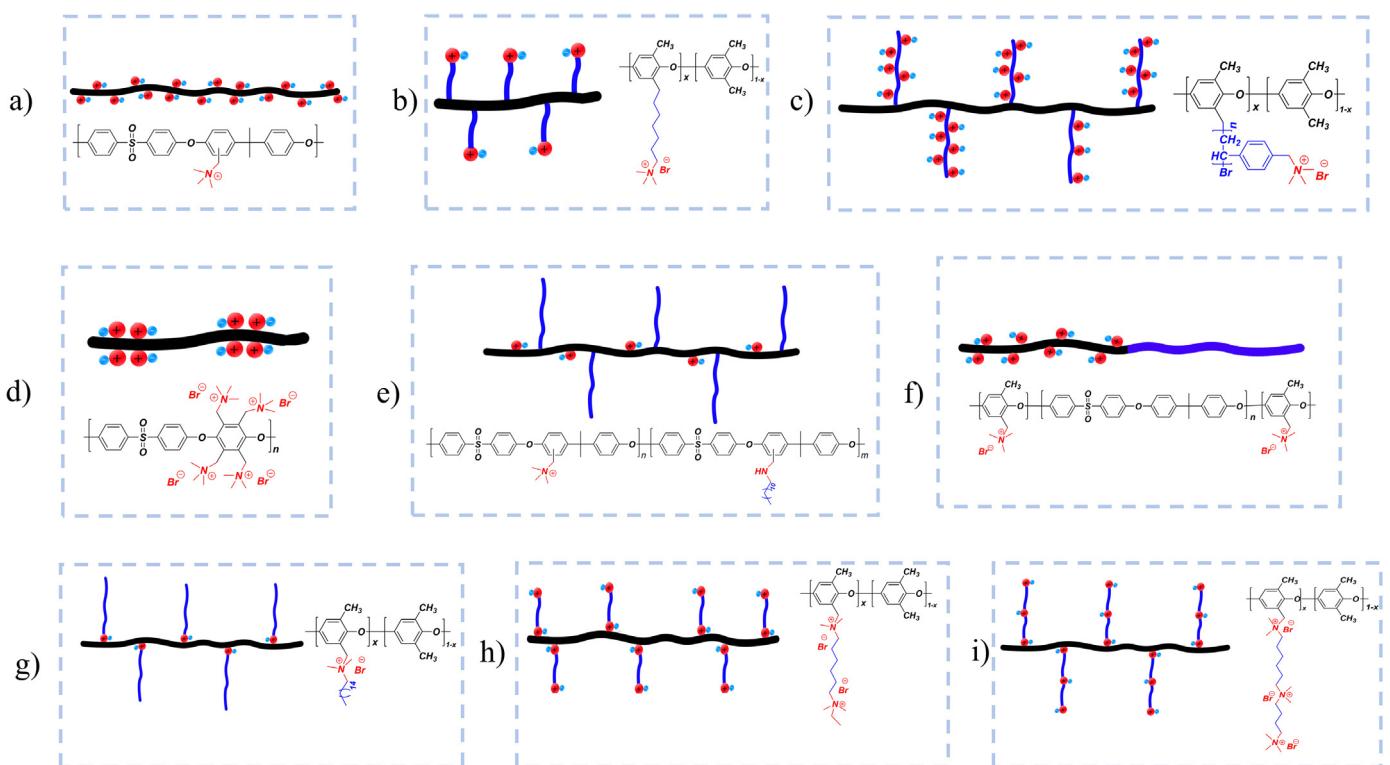
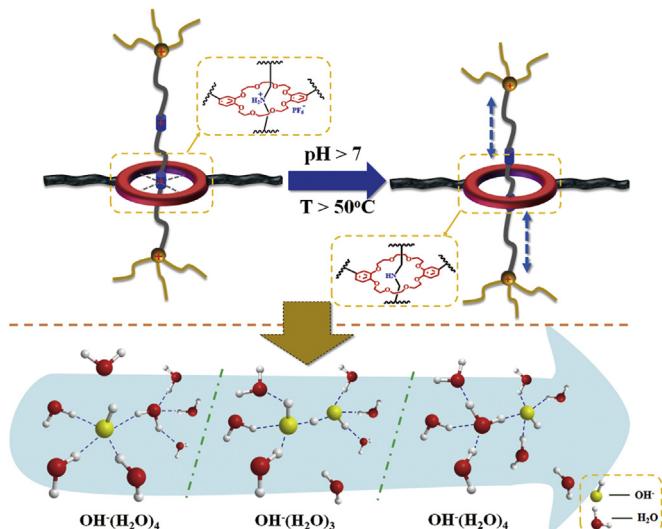


Fig. 5. Polymer architecture and representative chemistry schemes of anion exchange membranes.

Fig. 6. Schematic illustrations of comb-shaped polymer architecture containing mobile ion shuttles and hydroxide ion (OH<sup>-</sup>) transport via the continuous interconversion between hydration complexes (adapted from ref. [99]).

hydroxide conductivities occurs around 60 °C, which is ascribed to the thermally triggered shuttling dynamic behavior of the side chains, leading to enhanced mobility of hydroxide ions...

Similar to CEMs, comb-shaped AEMs (Fig. 5c) bearing locally and densely functionalized side chains were fabricated by our group in order to achieve good phase separation ability [100–103]. BPPO as a macro-initiator was grafted with N,N,N-trimethyl-1-(4-vinylphenyl)methanaminium chloride. These comb-shaped AEMs having high graft density and appropriate graft length presented excellent performance in hydroxide conductivity and alkaline tolerance. Encouraged by the positive result, our group continued to search for effective methods to facilitate the phase separation of AEMs [104]. Three QA groups were incorporated in the aliphatic

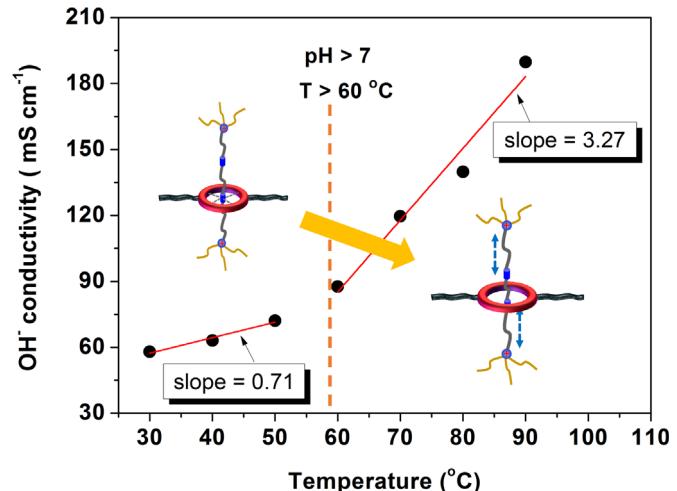


Fig. 7. Hydroxide conductivities of AEMs with “free shuttling” side chains as a function of temperature (reproduced from ref. [99]).

side chains of AEMs. Ascribing to the high flexibility of side chain and increased hydrophilic-hydrophobic discrimination between the polymer backbone and ionic segments, excellent phase separation and high hydroxide conductivity of 69 mS/cm (at room temperature) were observed.

Dense grafting of ACGs (Fig. 5d) on particular segments of polymer main chains is also an effective strategy to enhance the anion conductivity of AEMs [105–107]. Hickner and co-workers [108] synthesized highly conductive AEMs by poly-condensation of dense benzylmethylated biphenyl monomers followed by bromination and quaternization. The existence of distinct ion clusters, which was proved by small angle X-ray scattering (SAXS), is responsible for its excellent performance. Bai and co-workers [109] synthesized an AEM bearing one pendant tri-cation functionalized phenyl ring via multi-step reactions. Greatly enhanced hydroxide

conductivity was observed. Jannasch and co-workers [106] synthesized multi-block copolymers, which had single dioxyphenylene ring functionalized with two, three or four QA groups. The authors studied the influences of ion concentration and distribution on anion conductivity. Surprisingly, anion conductivity decreased with increasing local density of ionic groups, which was probably caused by the reduced ion-dissociation ability ascribed to increased proximity of the QA groups.

Zhuang and co-workers [110] demonstrated a simple and helpful route to enhance the anion conductivity of AEMs by introducing long aliphatic chains and QA moieties onto the polymer main chain (Fig. 4e). This unique polymer architecture was proven to be effective in improving the self-assemble ability of polyelectrolytes by coarse-grained molecular dynamics (CGMD) simulations. The results from TEM and SAXS showed the formation of “ionic highway”, giving rise to high hydroxide conductivity at relatively low IEC values.

Multi-block copolymers (Fig. 5f) have been applied in the field of AEMs in order to achieve high anion conductivity [97,111–114]. Bai and co-workers [115] synthesized an ABA tri-block copolymer by combining one block of PAES with two blocks of quaternary ammonium functionalized PPO. Because of the high hydrophilic-hydrophobic discrimination between different polymer segments, distinct phase separation was observed by SAXS, leading to enhanced hydroxide conductivity.

Rational polymer architecture design may solve the alkaline stability issue. Hickner and co-workers synthesized comb-shaped AEMs by reacting BPPO with long aliphatic chains, which were substituted by tertiary amine (Fig. 5g) [22,116,117]. Because of the steric hindrance effect and hydrophobic nature of this long aliphatic chain, which prevent the hydroxide ions from attacking QA groups, excellent long term alkaline stability was observed.

Apart from the decomposition of ionic moieties via nucleophilic attack by hydroxide ions and Hoffman elimination, the degradation of polymer backbone of AEMs is becoming one of the most major research themes in recent years [118]. Hickner and co-workers [119] investigated the influence of QA groups on the chemical stability of different polymer backbones. It was found that PES based AEMs undergo severe decomposition when exposed to strong alkaline environments. That was due to the strong electro-withdrawing effect from QA and sulfone groups. In this regard, a long spacer introduced between the QA groups and polymer main chains may effectively minimize the influence of QA groups on the chemical stability of polymer main chains [120,121]. Besides, decreasing the grafting ratio of positively charged QA groups also alleviates the fracture of polymer backbone. Zhuang and co-workers [122] designed unique polyelectrolytes functionalized by dual-cation containing side chains (Fig. 5h). Alkaline stability of this AEM was improved by allocating two QA groups into one side chain due to decreased grafting ratio of ionic group. Afterwards, our group reported a series of AEMs functionalized by multi-cation containing side chains. Promising nano-phase separation morphology as well as good alkaline tolerance were observed (Fig. 5i) [104,123]. Yan and Hickner reported AEMs having side chain linking densely functionalized side chains [124,125]. Both of these AEMs possessed sufficient alkaline tolerance, and desired IEC acquired at quite low grafting ratio.

### 2.3. Monovalent ion perm-selective membranes (MIPMs)

A monovalent ion perm-selective membrane (MIPM) allows for rapid permeation of mono-valent ions, while blocking passage of multi-valent ions. Owing to the special functions of MIPMs in distinguishing mono-valent and multi-valent ions with the same charge, they are widely explored in a wide range of applications including seawater desalination [126], acid recovery in

hydrometallurgy [127] and removal of specific ions from liquid waste [128]. The perm-selectivity between ions of the same charge in a mixture through MIPMs is governed by several factors, such as differences in ions' hydrated radii, affinities with IEMs and migration speeds in the membrane phase [129,130]. The strategies used for regulating such factors have been reported in the literature. Some of these strategies are as follows.

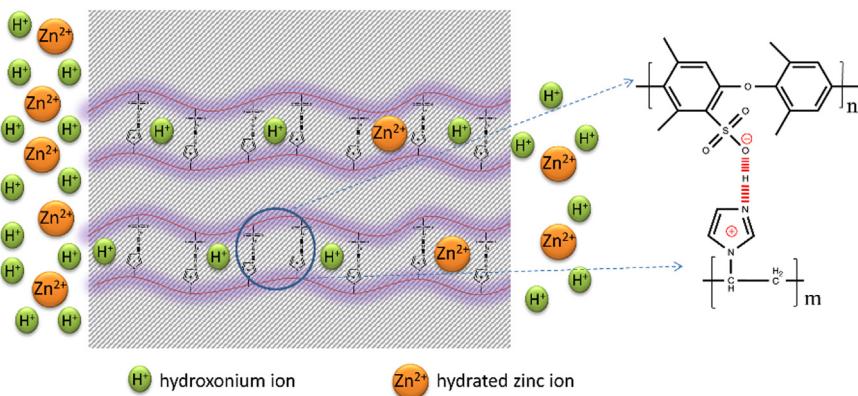
(1) Importing cross-linked moieties in IEM matrix or coating a cross-linked thin layer on the membrane surface is considered to be effective in obtaining MIPMs. With the introduction of cross-linked components, the IEM becomes denser. Therefore, the ions with different hydrated radii may be differentiated based on a size sieving effect. Apart from widely reported covalent cross-linking, acid-base cross-linking also demonstrates effective in improving the density of membrane matrix to obtain MIPMs. For example, an MIPM with this type of cross-linking was constructed by our group using imidazole groups and sulfonic acid groups (Fig. 8) [131]. The formation of hydrogen bonding networks based on the acid-base interaction makes the membranes more compact and also holds the ability to limit the passage of  $Zn^{2+}$ . Meanwhile, the channels along with the hydrogen bonding networks promote the transfer of  $H^+$ , leading to desired high  $H^+$  flux. Crystalline is another type of cross-linking. Recently, our group completed the preparation of a MIPM by adding crystalline domains into IEMs [132].

Although cross-linking is especially fascinating in preparing MIPMs, high electrical resistance caused by the cross-linking is an inevitable issue [132,133]. To decrease the detrimental influence of cross-linking, conducting layers are introduced onto the MIPM surface. Gohil and co-workers [134] developed a MIPM by means of the polymerization of pyrrole on the membrane surface. The poly-pyrrole layers could both reject multi-valent ions and reduce the resistance during the electrodialysis operation [135].

(2) Depositing an oppositely charged layer relative to the nature of bulk IEM' charge also enables the preparation of MIPMs. For this type of MIPMs, multi-valent ions with the same charge as the membrane surface are rejected due to the relatively large electrostatic repulsion, while mono-valent ions are still able to pass through the skin layer. Lambert et al. [128] modified a Nafion® membrane by electro-depositing highly protonated polyethyleneimine (PEI) on its surface. The PEI layer is positively charged in acidic media and has the potential to block the passage of multi-valent ions. More recently, with the development of layer-by-layer (LBL) technique, alternating adsorption of poly-cations and poly-anions has become a potential method to form an ultrathin layer for repelling multi-valent ions. For example, S. Muhyati et al. [136] deposited poly(sodium 4-styrene sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) alternatively on a NEOSEPTA AMX membrane by the LBL technique. With the increasing number of layers, the selectivity for the mono-valent anions is greatly improved.

Polymerization grafting of cationic/anionic vinyl monomers on the membrane surface is also an attractive option to obtain MIPMs through the surface modification means. Ogumi et al. [137] prepared monovalent cation perm-selective membranes by surface polymerization of 4-vinylpyridine monomers initiated by the generated radicals during the oxygen plasma treatment. The resultant membrane showed high monovalent cation perm-selectivity and low membrane resistance.

(3) Regulating the compositions of ionic functional groups and IEM matrices can be applied in achieving selective permeation of mono-valent ions. This is due to the fact that the perm-selectivity among ions with same valence state is not only governed by the difference in size, but also decided by the difference in affinity forces of ions with the membranes [129,138]. Nagarale et al. [139] investigated a series of CEMs having different functional groups including sulfonic acid, phosphonic acid, and carboxylic acid



**Fig. 8.** Constructing  $\text{H}^+$  transfer channels through the formation of acid-base pairs (adapted from ref. [131]).

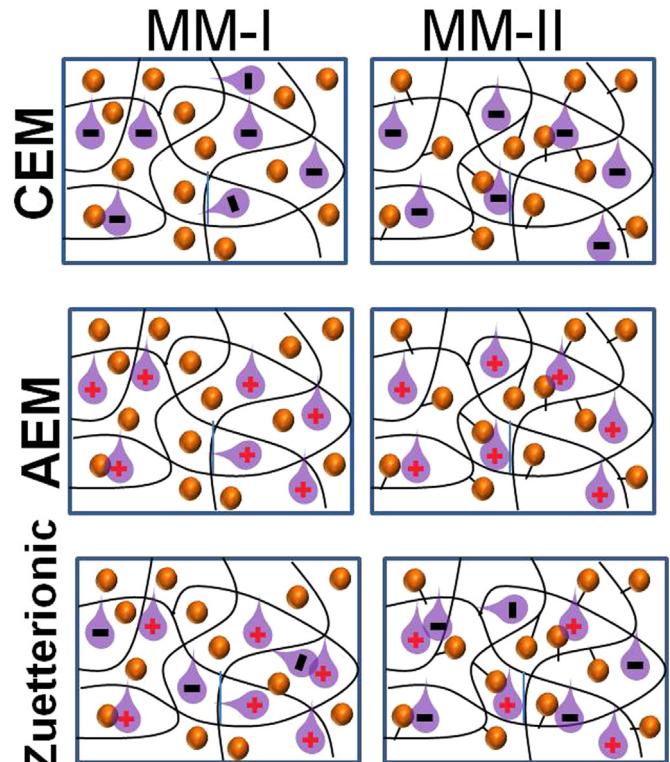
groups. The results showed that an IEM with phosphonic acid groups is the most suitable for the electro-driven separation of ions with identical charges. Furthermore, a few recent studies tried to prepare MIPMs by varying the hydrophobic and hydrophilic characters of the membranes. For example, Gohil et al. [140] adjusted the hydrophilic-hydrophobic property of pristine sulfonated PES by adding sulfonated poly(ether ether ketone) (SPEEK). It was observed that the perm-selectivity of mono-valent ions relative to di-valent ions increased with decreasing SPEEK contents.

The above-mentioned methods may be combined in a reasonable way to improve the monovalent perm-selectivity of IEMs. Although a large number of optional IEMs are widely reported in various industrial fields, the comprehensive properties of MIPMs can still not meet some requirements set for applications on an industrial scale. The limitations rely on low perm-selectivity, insufficient ion flux, and high electrical resistance. More research attention should be given to further improve the membranes.

#### 2.4. Mixed matrix membranes (MMMs)

Mixed matrix membranes (MMMs), in which inorganic components are embedded into organic polymers, are more advantageous in designing high performance IEMs because they combine the advantages of both polymers and inorganic materials [141]. The characteristics of MMMs are decided by the mixed components, nature of the interactions between organic and inorganic phase or distribution of dispersed phase. A variety of polymers have been chosen as continuous phase due to their flexibility, adjustable IEC and processing ability, whereas inorganic particles such as metal oxides, metal phosphates, graphene oxide (GO) and carbon nanotube (CNT) are dispersed into the polymer matrices to enhance thermal and mechanical stability as well as incorporate desired electrochemical properties [142]. As shown in Fig. 9, particles (inorganic moieties) can be dispersed in polymer matrices through mechanical doping of the particles (MM-I) or in-situ generation of the particles and linking them on polymer backbone through a chemical bond (MM-II). The preparation methods for MMMs include sol-gel process, blending, intercalation, in-situ polymerization, and molecular self-assembly [143]. The sol-gel process is especially helpful for preparing MMMs because it is easy to handle and can reach homogenous and fine distribution of inorganic particles [144].

In our group, cation exchange MMMs of sulfonated poly(2,6-dimethyl-1, 4-phenyleneoxide) (SPPO) and polyvinyl alcohol (PVA) have been widely studied. Modification of SPPO through the sol-gel process results into MMMs, which have high resistance to alkaline conditions and have enhanced thermal, mechanical and dimension stability. One such example is the preparation of MMMs by the sol-gel process of multi-alkoxy silicon copolymers



**Fig. 9.** Schematic illustration of MMM with particle doped in polymer matrix (MM-I) and particles dispersed in polymer matrix through chemical bonding (MM-II).

(poly(vinyl benzyl chloride- $\gamma$ -methacryloxypropyl trimethoxy silane)) (poly(VBC-co- $\gamma$ -MPS)) in the presence of SPPO [145]. The membrane swelling was reduced by increasing the content of poly (VBC-co- $\gamma$ -MPS). A similar strategy was applied to PVA in order to fabricate PVA based MMMs [146]. PVA incorporated with vinyl-trimethoxysilane (VTMS) and sodium allylsulfonate to increase the cation exchange groups showed strong alkaline stability [147].

MMMs are advantageous for fabricating tunable properties using different components. Cation exchange-MMMs were prepared from SPPO, PVA and tetraethoxysilane (TEOS) [148]. The double organic phases of PVA and SPPO were expected to combine their advantages regarding their organic solvent resistance and ion exchange properties. To achieve dense membranes, the SPPO phase was encapsulated into PVA/SiO<sub>2</sub> matrix, which resulted in a diminished degree of cross-linking PVA/SiO<sub>2</sub> matrix.

AEMs are less developed than CEMs due to the difficulty in preparing cationic groups fixed in polymers and the intrinsic

nature of low mobility of anions. AEMs based on mixed matrix morphologies have not only been proposed to improve mechanical and thermal stabilities, but also enhance the chemical resistance. Blending of quaternized vinylbenzyl chloride (VBC) copolymers, monophenyltriethoxysilane (EPH) and  $\gamma$ -methacryloxypropyl trimethoxy silane ( $\gamma$ -MPS) through the sol-gel reaction results in AEMs having strong alkali resistance, excellent thermal and mechanical stabilities. To improve the membrane preparation toward high ion exchange capacity, a multi-step sol-gel processing procedure was found to increase the homogeneity of the resulting membrane. For example, AEMs prepared from multi-alkoxy precursors of glycidylmethacrylate (GMA) copolymers,  $\gamma$ -MPS, N-triethoxysilylpropyl-N,N,N-trimethylammonium iodine and EPH exhibited higher alkali resistance and good mechanical strength at high IEC [149]. The optimum dimensional stability was achieved by using UV/thermal curing [150]. In this regard, the properties of MMMs can be adjusted by controlling the polymer's molecular weight, silica content and temperature during the heat treatment.

Although MMMs are comparatively more advantageous in improving mechanical and thermal stabilities than the polymeric IEMs, completing homogeneity on a molecular-scale remains challenging. On the other hand, the interface between organic and inorganic phases should be studied in detail, since it is crucial to the characteristics of MMMs. The studies on these aspects deserve more research efforts.

## 2.5. Bipolar membranes (BPMs)

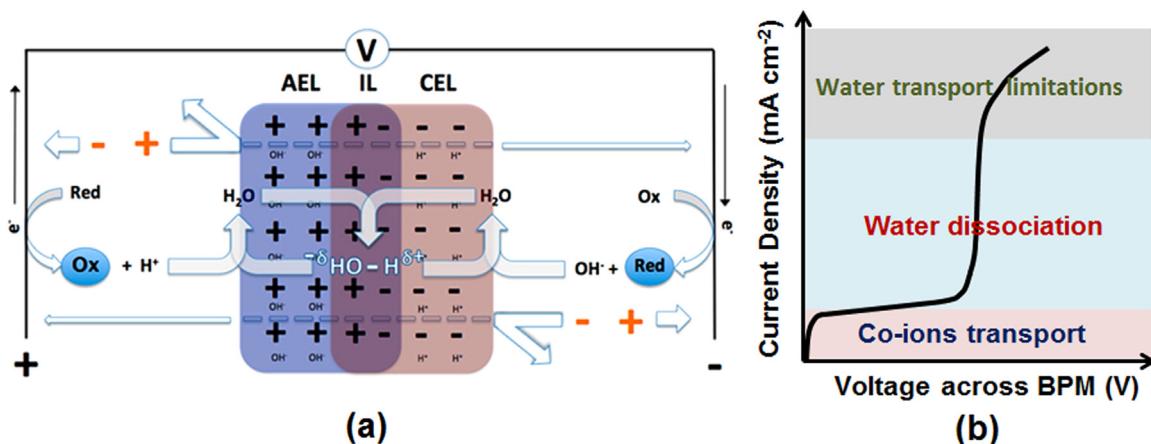
Over the last decade or so, IEMs have evolved from a laboratory tool to industrial products with significant technical and commercial impacts [151,152]. Among these IEMs, the bipolar membrane (BPM), which is composed of one cation exchange layer (CEL), one anion exchange layer (AEL) and an interfacial layer (IL) between the two layers, occupies a special position due to its ability for generating protons and hydroxide ions from water molecules under direct current polarization. In 1956, this type of IEM was referred to as BPM in an academic literature for the first time [153]. Since then, intensive studies have been conducted on BPMs, which focus on a number of BPMs' industrial applications, such as electrodialysis for environmentally clean technologies and treatment of salt water effluents. It is worth mentioning that a well-established milestone in this field is the understanding of the mechanism of electric field enhanced (EFE) water molecule dissociation in BPMs [154–156].

BPMs are analogous to p-n junction semiconductors, whereas the junction formed at the BPM interfacial layer (IL) constitutes a

depletion region and thus contains a built-in potential [158,159]. Fig. 10a shows a schematic illustration of the structure and function of BPMs. When a potential ( $> 0.83$  V) is applied across the membrane, a very large electric field ( $10^8$  V/m) is generated in the IL. The water molecules residing in the IL become sufficiently polarized and hence, get dissociated [157,160]. Fig. 10b shows a typical steady current density-voltage (I-V) curve, which presents the operation of a BPM. The curve clearly presents the water splitting process during the passage of an increased current density through the membrane [158,161]. In the first region, the current is very low and is mainly transported by the diffusion of salt ions. In the second region, water dissociation occurs and the current is transported by protons and hydroxide ions, which are generated in the interphase. In the third region, the generation rate of protons and hydroxide ions is limited by the transport of water molecules into the interphase, leading to an increase of the operating voltage and the destruction of the membrane. It is worth mentioning that the water dissociation in the BPMs is seven orders of magnitude higher than that in the free solution. The actual water dissociation mechanism is still not fully understood and needs extensive research attention.

Various mechanisms have been proposed to explain the accelerated water dissociation in BPMs. A well-established mechanism, which is supported by theoretical and experimental evidences, is the so-called reversible proton transfer reaction mechanism [154,155]. According to the model, the generation of protons and hydroxide ions at the interfacial region are believed to be the result of protonation and deprotonation of the reaction between the water molecules and fixed charge groups. This model can explain the acceleration of water dissociation in the interphase of BPMs and also serve as a theoretical basis for the development of BPMs.

Typically, BPMs have been commonly prepared by LBL casting of CEL and AEL materials, or pasting CEL and AEL together by external addition of heat and pressure or by using adhesives. During these processes, a thin, modified IL is formed between CEL and AEL to generate protons and hydroxide ions. Available materials for both CEL and AEL need to transport ions effectively. The water dissociation materials for the IL are sought to control the BPM potential to a value as close to the thermodynamic potential of 0.83 V as possible so that the energy consumption could be reduced. The chemical composition and structure of the IL are elaborately designed, following the mechanism of the proton transfer reaction. One promising strategy is to immobilize catalysts in the IL to provide alternative reaction paths for the dissociation reaction by forming very active complexes. Previous studies have reported that weak acid and base with an equilibrium constant close



**Fig. 10.** Schematic illustrations of (a) the structure and function of a BPM (adapted from ref. [157]); (b) a typical I-V curve of a BPM in a salt solution (adapted from ref. [158]).

to that of the water dissociation reaction constant  $pK_a = 7$ , e.g. amino groups (primary, secondary or tertiary amine) [154], and pyridines [162] could be incorporated into the IL. Our previous work have demonstrated the catalytic activities of hydrophilic macromolecules, including polyethylene glycol (PEG) [163], PVA [164], and hyper-branched polymers [165]. Additionally, inorganic substances, such as GO [157], and heavy metal ions complexes [166] could also been incorporated into IL for enhancing the water dissociation.

In summary, tremendous progresses have been made in screening suitable catalysts for the water dissociation and improvement of membrane preparation techniques in the past several decades. It is worth mentioning that high performance commercial BPMs are available and are widely used in industrial scale application. However, there are still a lot of open questions regarding the development of chemical stable polymer candidates, precise control of micro-morphology and in-depth understanding of water dissociation and ions transport mechanism within BPMs. In practical applications, BPMs are required to possess low electrical resistance at high current density, high water dissociation ratio, low co-ion transport rate, high ionic selectivity, and most importantly, good chemical stability against acid and base due to direct contact of CEL with the acid solution and that of AEL with the alkaline solution. However, highly alkaline stable AEL candidates are rarely reported. Additionally, precise control of thickness and architecture of the catalytic interphase is still unsatisfactory. Further systematic studies on these points will continue to push forward the industrial application of BPMs.

### 3. Preparations

In addition to synthesizing new materials having promising properties for IEMs, suitable preparation methods are of equal importance to guarantee the quality of resulting IEMs. The typical process for obtaining an IEM involves dissolving the above-mentioned materials in strongly polar solvents, casting IEM solutions onto a leveling plate, and finally, evaporating the solvents. To date, this method is still widely used for getting access to IEMs. Meanwhile, there are emerging new preparation methods used to improve the structure and properties of IEMs.

#### 3.1. Polymer blending

Polymer blending is a very attractive method to prepare IEMs, since it can combine outstanding characteristics of each component while overcoming the deficient characteristics of a single component. The method not only increases the stability, selectivity and ion conductivity of IEMs, but also reduces the cost and swelling [167].

In the field of IEMs, two general strategies are used to blend polymers: fluorinated and non-fluorinated polymers blending, and functional and non-functional polymers blending. Fluorinated polymers are very famous for preparing IEMs due to their high chemical stability and excellent membrane forming ability. However, high cost and excessive hydrophobicity restrict their use in the area of IEMs. Non-fluorinated materials are relatively cheap, but they have insufficient stabilities, which prevent them from indispensable applications. Blending these two kinds of materials to prepare IEMs has been considered as a convenient, efficient and potential approach to improve the performances of IEMs [168–171]. Ion functionalized polymers always facilitate the enhancement of ionic conductivities by constructing water channels, whereas excessive ionic groups may lead to mechanical failure. Therefore, adding some kinds of hydrophobic polymers is a very useful approach to restrict water swelling and enhance stabilities

of IEMs. Versatile materials are used for these two general strategies. Among them, polytetrafluoroethylene (PTFE), PVDF, PS and its co-polymers [172], PPO [173], PES [174], PVA [175], poly(ether ether ketone) (PEEK) [176–178], PBI [179,180] and polyaniline (PAN) [181,182] have been widely researched in recent years.

Polymer blending provides various possibilities to regulate the properties of IEMs [168]. By controlling compositions of two or more kinds of polymers, many properties such as ion conductivities, water swelling and chemical stabilities could apparently be enhanced. However, the compatibility of different components remains challenging, which might render blending IEMs to exhibit poor mechanical properties due to excessive interfaces. Qiao *et al.* [183] tried to solve this problem by adding polyvinyl pyrrolidone (PVP) as a stabilizer. The highest proton conductivity of the resultant membrane reached at 0.088 S/cm at 25 °C, which is close to that of Nafion®, indicating that PVP acts as an efficient adhesion agent. In our lab, polymer blending was explored to fabricate PPO based membranes. The chloroacetylation of PPO (CPPO) prepared for AEMs often possesses extremely low hydrophilicity, resulting in low ionic conductance. BPPO was thus blended with CPPO to enhance the hydrophilicity after quaternization. The membranes exhibited high hydroxide conductivities (0.022–0.032 S/cm at 25 °C) and low methanol permeability ( $1.35 \times 10^7$  to  $1.46 \times 10^7$  cm<sup>2</sup>/s) [173].

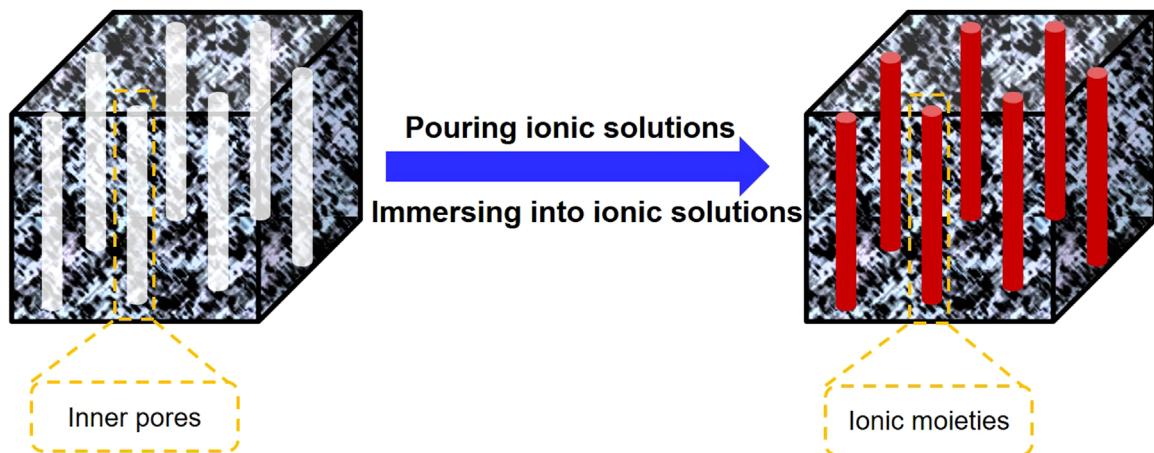
Polymer blending, although simple but a fascinating way to rectify the shortcomings of a single component, can widely be used for improving the IEMs' performances. Mixing two or more polymers in an appropriate ratio is the key to their successful use in the field of IEM, which can achieve synergistic effects in the resulting IEMs. In this regard, further research efforts are still underway.

#### 3.2. Pore filling

Pore filling is a novel method to prepare IEMs with low swelling and high selectivity. To prepare IEMs using a pore filling method, the most important prerequisite is to search for appropriate porous substrates. A porous substrate is required to be chemically inert and mechanically stable, and thus the expansion of soft electrolyte polymers in pores can be restricted by the hard matrix [184]. For IEMs, some of the available substrates involve porous PAN [185], high-density polyethylene (PE) [186], polypropylene (PP) [187], PES [188], and PI [189]. The pores are constructed by track etched or phase inversion methods [190,191]. Apart from polymeric substrates, inorganic materials, such as porous alumina can also be used for obtaining pore filling IEMs [192]. For inorganic substrates, the pore size distribution is uniform and the pore is small enough compared to polymeric substrates, leading to higher selectivity.

Pore filling IEMs are generally prepared by introducing polymeric electrolytes into the porous substrates (Fig. 11). The simplest way to achieve this process is pouring the selected ionomers on the surface of membranes [193]. The electrolytes flow into the inert pores and an IEM can be formed when the volatilize solvents are completely evaporated. To ensure successful preparation, relatively concentrated solutions having sufficient viscosity are favored for retaining the polymers inside pores. Occasionally, the process should be repeated several times to guarantee the formation of "defect free" IEMs. Immersing porous substrates into the ionized polymers is another effective way to prepare this type of membranes, and is called the pore soaking technique [194]. The basic principle behind the pore soaking technique is always similar to that of the pore filling technique.

In this method, Masatoki Ito and co-workers [189] prepared CEMs by impregnating copolymers of poly-2-acrylamide-2-methylpropanesul-phonic acid (PAMPS) and PSS into a porous PI



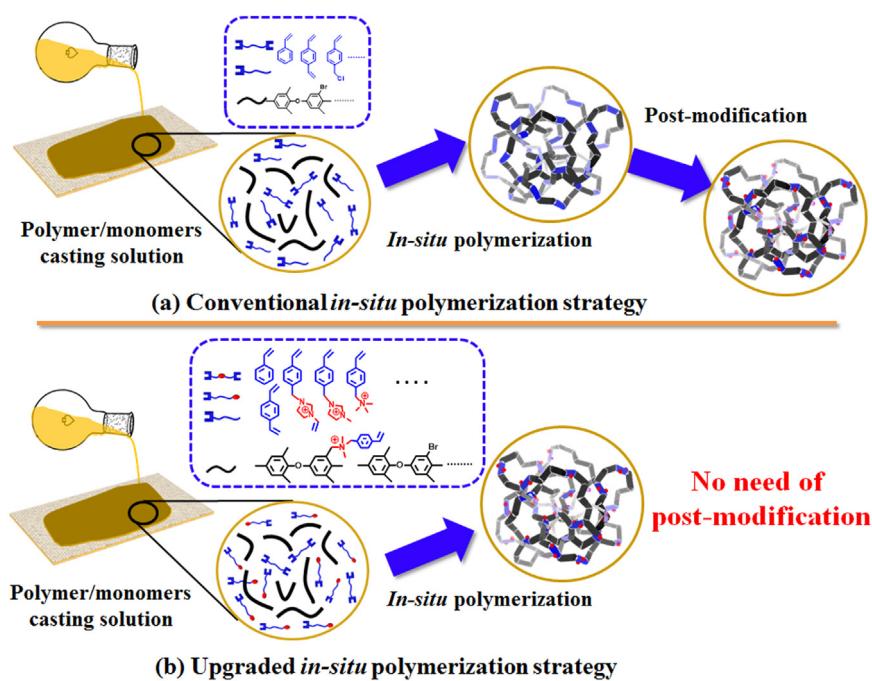
**Fig. 11.** Schematic illustrations of preparing IEMs with pore fill or pore soaking technique.

substrate. Analogously, Young-Woo Choi and co-authors developed AEMs, which consisted of a cross-linked polymer with N,N'-bis (acryloyl) piperazine and (vinylbenzyl) trimethylammonium chloride in a porous polyolefin substrate [195]. The resulting membrane reached extremely high IECs within the range of 3.78–4.45 mmol/g without excessive swelling. Apart from polymeric IEMs, the organic-inorganic composite membranes are also developed using this route. For example, a PVA-GO nano-hybrid layer was poured onto an asymmetric PAN ultrafiltration membrane, and a “pore filling” composite membrane was obtained by the subsequent hydrolysis of the nitrile groups on the PAN [196].

Pore-filling and pore-soaking technique have been broadly developed and used for preparing IEMs over the past ten years. The methods offer diverse possibilities for fabricating IEMs having different substrates and functional polymers. Up till now, most of the studies have focused on the choice of ionic substances and porous substrates, while efforts focusing on how to decrease the leaking of ionic materials are still in their infancy. The membranes prepared by these methods should guarantee long-term use without the decline of their properties.

### 3.3. In-situ polymerization

Traditional preparation of IEMs usually employs modification of pristine polymers or direct polymerization of functionalized monomers. In these approaches, a large amount of organic solvents used during both the reaction and membrane formation processes will bring toxicity risks to the environment. Hence, to achieve industrial-scale manufacture, it is important to develop simple, rapid and environmental friendly methods for preparing IEMs. Recently, a solvent-free strategy using in-situ polymerization has been reported to overcome the obstacles encountered in solvent aided polymerization [197–200]. The strategy is different from the above mentioned post-modification and direct polymerization techniques, in that the organic solvents are replaced by liquid monomers, which are fully incorporated into the resultant membrane. This typical strategy has been illustrated in Fig. 12(a). Previously, thermally stable CEMs have been prepared according to this strategy by dissolving PPO or BPPO in liquid monomers, rather than the organic solvent, followed by in-situ polymerization to obtain un-charged membranes. A post-modification, such as the



**Fig. 12.** Schematic illustrations of (a) conventional and (b) upgraded in-situ polymerization strategies for preparation of IEMs.

sulfonation reaction, was performed to further introduce the sulfonate anions. The resultant membrane exhibited a proton conductivity of around 70 mS/cm under 100% humidity and at room temperature, which is close to that of the corresponding value for Nafion® 117 under identical conditions (around 80 mS/cm). The dimensional change ratio of the membrane was below 3%, which is much lower than that of Nafion® 117 [197].

The above method was further upgraded such that there was no need for the post-modification process. This approach consists of simultaneous in-situ polymerization and quaternization (schematically presented in Fig. 12(b)). Firstly, BPPO is dissolved in the liquid monomers' mixture of VBC and styrene without any organic solvents. Then, appropriate amounts of N-vinylimidazole and N-methylimidazole are added to introduce imidazolium cations. The transparent, robust and cross-linked AEMs were obtained by thermal crosslinking of the un-saturated moieties during the formation process of the membrane. Particularly, imidazolium cations located at the cross-links provide the resultant membrane with a high IEC (over 2.0 mmol/g) for target low area resistance (lower than  $1.4 \Omega/\text{cm}^2$ ), while maintaining the high stability as well as ion selective transport property. The subsequent membranes exhibited much higher limiting current densities (over 20 mA/cm<sup>2</sup>) than the commercial AEM (Neosepta AMX; 14.2 mA/cm<sup>2</sup>; measured under the same condition) [201].

In-situ polymerization without post-functionalization was firstly developed by our group, whereas its development is still at an early stage. In-situ polymerization acts as a versatile, feasible, and environment-friendly method for preparing robust IEMs and should deserve more research attention. Especially, this promising method should be extended to prepare CEMs, by selecting monomers having cation conductive groups and sufficient polarity to dissolve polymers.

#### 3.4. Electro-spinning

The method of electro-spinning offers unique advantages of producing electrospun nanofibers with diameters on a nano-scale, which possess attractive characteristics including three dimensional networks, fully interconnected pores, high porosity and large specific surface area [203,204]. Additionally, electrospun nanofibers were found to exhibit higher tensile modulus compared with the bulk [205]. The electro-spinning method has

attracted research extensive attention to improve the performances of CEMs and AEMs in several applications [206–208]. By electro-spinning quaternized PPO (QPPO)-SiO<sub>2</sub> mixed solutions, composite nano-fibrous mats were prepared having an average diameter of 100 nm, which were subsequently treated with hot pressing to achieve the preparation of nano-fiber AEMs (this process and the resultant membranes are shown in Fig. 13) [202]. Owing to their large specific surface area and high porosity, the resulting AEM exhibited seven times higher separation efficiency towards acid and metal ions compared with the bulk AEM having a similar IEC. Similarly, SPPO based nano-fiber CEMs were explored for alkali recovery, resulting in significantly increased selectivity of the membrane [209]. Despite its fascinating advantages, the electro-spinning method has still only be applied on laboratory scale. It urgently needs to be explored in depth to tailor IEMs from various polymer structures and functional groups.

#### 4. Commercialization of ion exchange membranes

Scientific progresses in IEMs pave the way for their commercialization. Various types of available commercial IEMs have been delivered by internationally famous IEM manufacture companies. Currently, FuMA-Tech GmbH in Germany, ASTOM Co., Asahi Glass Co., Ltd. in Japan, and DuPont Co. in America account for a lot of the market share of IEMs. Particularly, Nafion™ perfluorinated CEMs yielded by DuPont Co. belong to highly efficient fuel cell membranes, promoting the commercialization process of fuel cells. fumasep® IEMs produced by FuMA-Tech GmbH, Selemion® IEMs produced by Asahi Glass Co., Ltd. and NEOSEPTA® IEMs produced by ASTOM Co. display high ion selectivity, low resistance, and sufficient chemical stability, have widely been used in electrochemical related processes.

In this decade, a majority of Chinese companies have also been engaged in IEM manufacture and plant construction in the field of membrane technology for the treatment of water and process solutions. Among them, Hefei Chemjoy Polymer Materials Co. Ltd., Shandong Tianwei Membrane Technology Co. Ltd., and Beijing Tingrun Membrane Technology Co. Ltd., are currently clear leaders that can provide top quality products with high selectivity, low resistance, and good physical properties. To date, they have delivered essential science and technology to resolve the nation's

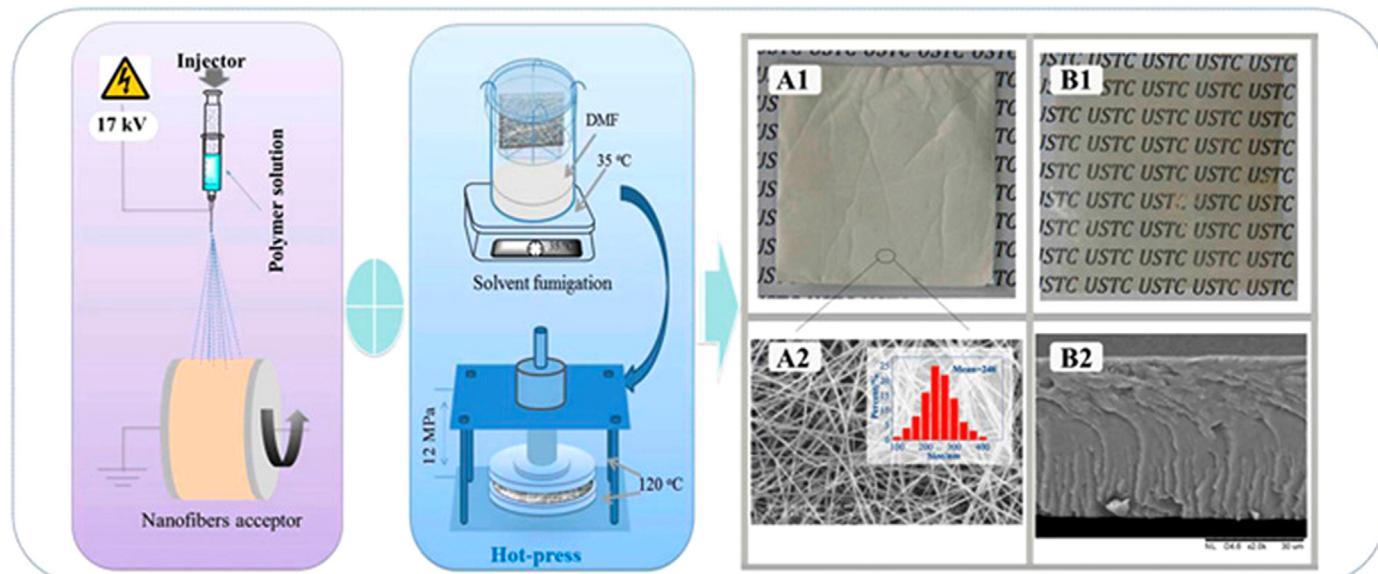


Fig. 13. Schematic illustrations of the electro-spinning process and SEM images and optical photograph of the resulting AEMs (reproduced from ref. [202]).

**Table 1**

The properties of commercial IEMs from famous membrane companies.

Company	Name	Type	Thickness (mm)	IEC <sup>a</sup> (mmol/g)	R <sub>m</sub> <sup>b</sup> ( $\Omega \text{ cm}^2$ )	V <sub>diss</sub> <sup>c</sup> (V)	Applications
<b>FuMA-Tech GmbH, Germany</b>	fumasep <sup>®</sup> FKB	CEM <sup>d</sup>	0.10–0.13	1.2–1.3	4–6	—	Desalination
	fumasep <sup>®</sup> FAB	AEM <sup>e</sup>	0.10–0.13	1.0–1.1	4–7	—	Desalination
	fumasep <sup>®</sup> FKD	CEM	0.08–0.09	1.2–1.4	1.0–1.2	—	Base recovery
	fumasep <sup>®</sup> FAD	AEM	0.08–0.09	1.5–1.7	0.4–0.8	—	Acid recovery
	fumasep <sup>®</sup> FBM	BPM <sup>f</sup>	0.18–0.2	—	—	—	Production of acid and base
<b>ASTOM Co., Japan</b>	NEOSEPTA <sup>®</sup> CMX	CEM	0.17	—	3.0	—	Desalination
	NEOSEPTA <sup>®</sup> CMB	CEM	0.21	—	4.5	—	Base recovery
	NEOSEPTA <sup>®</sup> AMX	AEM	0.14	—	2.4	—	Desalination
	NEOSEPTA <sup>®</sup> AFN	AEM	0.16	—	0.5	—	Acid recovery
	NEOSEPTA <sup>®</sup> BP-1	BPM	0.22	—	—	1.2	Production of acid and base
<b>DuPont Co., USA</b>	Nafion <sup>TM</sup> N115	CEM	0.127	0.95–1.01	—	—	Fuel cell
	Nafion <sup>TM</sup> N117	CEM	0.183	0.95–1.01	—	—	Fuel cell
	Nafion <sup>TM</sup> N110	CEM	0.254	0.95–1.01	—	—	Fuel cell
<b>Asahi Glass Co., Ltd., Japan</b>	Selemion <sup>®</sup> CMV	CEM	0.13–0.15	—	2.0–3.5	—	Desalination
	Selemion <sup>®</sup> AMV	AEM	0.11–0.15	—	1.5–3.0	—	Acid recovery
	Selemion <sup>®</sup> ASV	AEM	0.11–0.15	—	2.3–3.5	—	Desalination
	Selemion <sup>®</sup> DSV	AEM	0.13–0.17	—	—	—	Acid recovery
<b>Chemjoy Co., Ltd., China</b>	Chemjoy <sup>®</sup> CJMCED	CEM	0.14–0.16	0.9–1.5	< 2	—	Desalination
	Chemjoy <sup>®</sup> CJMAED	AEM	0.14–0.16	0.9–1.2	< 4	—	Desalination
	Chemjoy <sup>®</sup> CJBPM	BPM	0.2–0.25	—	—	≤ 1.8	Production of acid and base
<b>Tianwei Co., Ltd., China</b>	TWEDC	CEM	0.10–0.13	—	< 4	—	Desalination
	TWEDA	AEM	0.13–0.16	—	< 4	—	Desalination
	TWBPI	BPM	0.18–0.23	—	—	≤ 1.8	Production of acid and base
<b>Tingrun Co., Ltd., China</b>	JCM-II	CEM	0.16–0.23	1.8–2.9	1–7	—	Desalination
	JAM-II	AEM	0.16–0.23	1.6–2.2	4–10	—	Desalination
	BPM-I	BPM	0.16–0.23	—	—	≤ 1.6	Production of acid and base

<sup>a</sup> IEC: Ion exchange capacity.<sup>b</sup> R<sub>m</sub>: membrane area resistance (0.5 mol/L NaCl, 25 °C).<sup>c</sup> V<sub>diss</sub>: water dissociation voltage (100 mA/cm<sup>2</sup>, 25 °C).<sup>d</sup> CEM: Cation exchange membrane.<sup>e</sup> AEM: Anion exchange membrane.<sup>f</sup> BPM: Bipolar membrane.

most challenging issues, such as acidic/basic waste water treatment, seawater desalination, cleaner production (Table 1).

## 5. Applications

Due to vast ion functional groups and selectively transport of ionic species while blocking neutral ones, IEMs are generally applied in separation and transport technologies. They are the indispensable components in some traditional processes, such as diffusion dialysis (DD), electrodialysis (ED), and bipolar membrane electrodialysis (BMED). More recently, IEMs have been extended to novel applications associated with energy conversion and production, including reverse electrodialysis (RED), fuel cells (FC), and redox flow batteries (RFB).

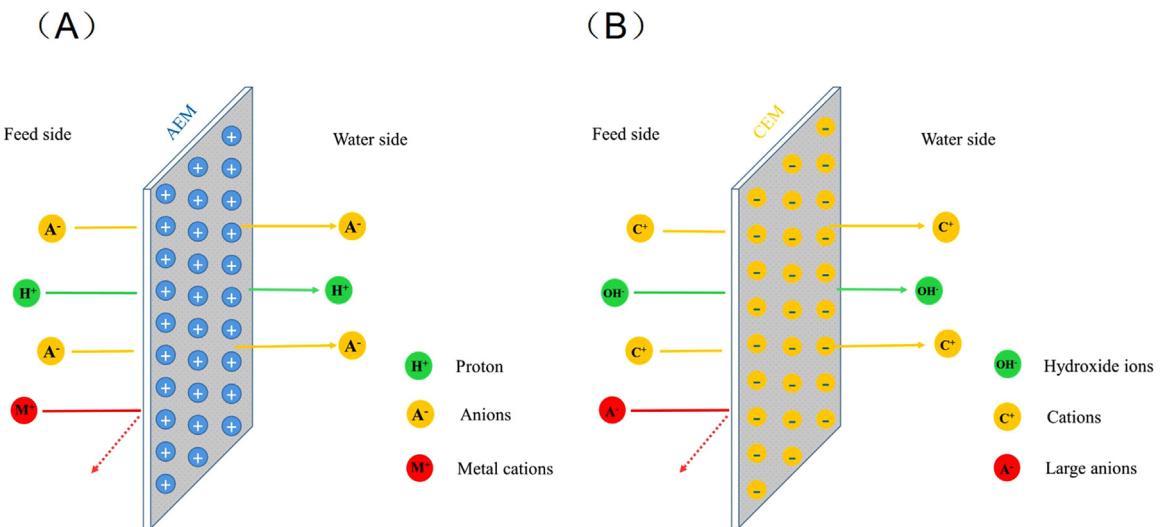
### 5.1. Diffusion dialysis (DD)

Diffusion dialysis (DD), which is also known as the concentration or natural dialysis, is an IEM based separation process driven by a concentration gradient across the membrane. Because of its low energy consumption and environmentally friendly characteristics, DD has widely been applied in the recovery of free acids or bases from spent treatment bath solutions in the surface finishing and textile processes. As a crucial component of the DD process, IEMs determine the performance of the DD process. DD can be classified into acid recovery diffusion dialysis (ARDD) and base recovery diffusion dialysis (BRDD) according to the type of IEMs employed therein (Fig. 14)..

#### 5.1.1. Acid recovery diffusion dialysis

In a typical acid recovery diffusion dialysis (ARDD) process, AEMs are used in a membrane stack for separating two different liquids: the acidic waste water and demineralized water. Anions (such as Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>) in the feed side can spontaneously permeate through the AEMs due to the concentration gradient, whereas the metal cations (such as Fe<sup>2+</sup>, Al<sup>3+</sup> and Zn<sup>2+</sup>) are retained. However, protons (H<sup>+</sup>) do not obey this rule. Their smaller size, lower valence state and higher mobility (as compared to the metal cations) allow them to pass through the IEMs together with anions to maintain the electrical neutrality. In order to efficiently obtain high purity of recovered acid on the water side, AEMs tailored for ARDD must possess the advantages of high H<sup>+</sup> permeability and good selectivity between the proton and other metal cations.

Laboratory scale AEMs referred in Section 2.2 can be successfully applied to ARDD. DF-120, which acts as the representative commercial scale AEM employing PPO as the polymer main chains, is demonstrated to be a promising AEM for recovering acids [210]. In order to enhance the proton flux (U<sub>H<sup>+</sup></sub>) of AEMs, the presence of sufficient ion exchange groups or assistant functional groups attached to the membrane matrix is compulsory. However, this will lead to compromise between flux and selectivity, which is called the trade-off effect. Attempts have been made to solve this trade-off effect by constructing porous structure within the membrane. Porous BPPO was prepared by multi-silica copolymers followed by quaternization [211]. The fabricated membranes possessed a porous support layer and contained multi-functional groups of -OH, -COOH, and QA groups. It is believed that both -OH and -COOH groups can facilitate the conduction of protons due to the formation of hydrogen bonds. Additionally, extremely high proton flux (U<sub>H<sup>+</sup></sub>) values (within the range of 0.020–0.025 m/h) for



**Fig. 14.** Schematic illustrations of the processes for: (A) acid recovery diffusion dialysis, and (B) alkaline recovery diffusion dialysis.

this porous AEM were observed at room temperature.

Despite numerous efforts devoted to the fabrication of AEMs for DD applications, ion conducting groups attached to the polymer matrix, which determine the transport of anions through the membranes, were all based on QA groups. Our lab has prepared DBU based AEMs (chemical details are given in Section 2.2) and investigated their performance in ARDD [64]. The basicity of DBU is quite high (pKa values of 12), which leads to improved dissociation ability of anions and the formation of anion-ion conducting group pair. This type of AEM thus achieved high anion permeability, resulting in good  $U_{H^+}$  values.

### 5.1.2. Base recovery diffusion dialysis

When DD is used for generating free base from basic waste water while using CEMs, this process is called base recovery diffusion dialysis (BRDD). An ideal CEM for BRDD should possess the advantages of high base permeability and good selective transport efficiency for  $OH^-$  over other anions. In our lab, MMMs were developed as excellent candidates for BRDD. The multi-alkoxy silicon copolymer in the presence of SPPO were firstly synthesized by our group [145]. High hydroxide ion flux ( $U_{OH^-}$ ) and good discrimination between  $OH^-$  and  $VO_4^{2-}$  were observed. In order to further enhance the base permeability of hybrid IEMs, our lab continued to prepare double organic phase hybrid CEMs composed of PVA/SPPO/SiO<sub>2</sub> [212]. It was observed that with the increase of SPPO content, higher  $U_{OH^-}$  values were obtained.

In short, the DD process is relatively simple and straightforward. The key to achieve desired properties using this process lies in choosing the appropriate IEM materials. In this section, the process is described and a few representative IEMs are presented. In fact, both the materials (mentioned in Section 2.1) and the preparation methods (shown in Section 3) can be combined to obtain high performance IEMs for DD processes. Moreover, an IEM having both acid and alkaline recovery functions should be explored as the next generation IEM specific for the DD applications. Importing auxiliary conductive groups into IEMs may be a feasible route. For example, zwitterion membranes, where cationic groups are deemed to be the auxiliary groups relative to the anionic groups and vice versa, are expected to turn into next generation IEMs for DD.

## 5.2. Electrodialysis (ED)

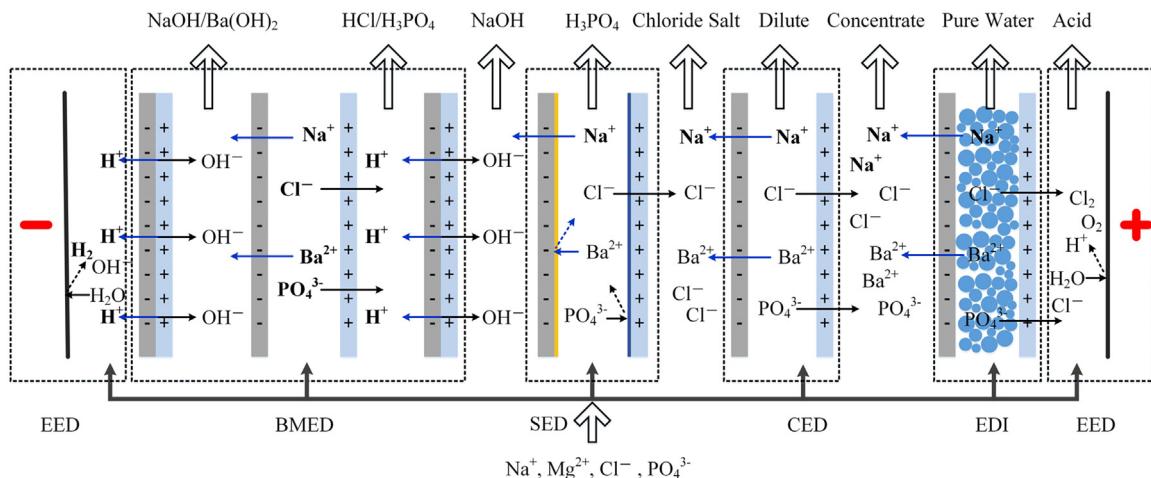
Electrodialysis (ED) is the state-of-the-art IEM process for water desalination and deionization in the chemical process industry. It can be divided into conventional electrodialysis (CED), bipolar

membrane electrodialysis (BMED), electro-electrodialysis (EED), selective electrodialysis (SED), two-phase electrodialysis (TPED), and electro-deionization (EDI) (as shown in Fig. 15). In this section, CED (termed as ED) is specifically discussed in detail..

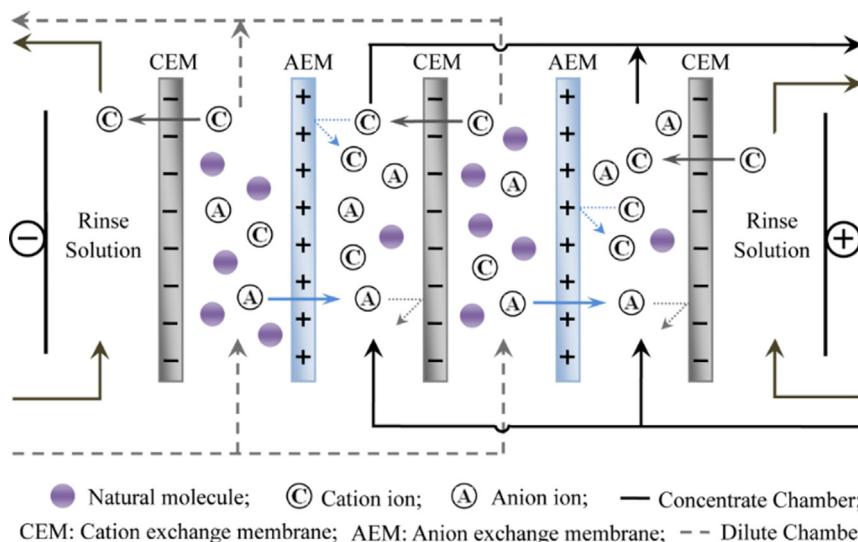
IEMs are used in ED to achieve salt removal/re-concentration. Cations move through CEMs with positive charges from dilute compartments to the concentrated ones. The process is consistent with the current field direction, and subsequently these cations are blocked by the negatively charged AEMs. Correspondingly, anions move in an opposite direction to maintain electrical neutrality of the whole system. Neutral molecules or small particles are retained in the feed solution. A typical ED system contains: (1) a power supply, (2) an electrodialysis stack combined with the auxiliary materials, such as spacers, electrodes, and gasket seal, and (3) IEMs sequentially arranged inside the stack (Fig. 16). Among different applications in which ED is used, parameters such as desalination ratio, feed recovery, re-concentration efficiency, water recovery efficiency, current efficiency, energy consumption and operating cost should be taken into considerations. The performance is normally affected by changing the feed concentration, current density, and membrane type. Among these, the supplied current needs to be controlled below the limiting current density. That is because the water dissociation occurs on the membrane interface once the limiting current density arrives. With the occurrence of this phenomenon, the consumed current is used for water dissociation instead of the effective ionic movement. In order to increase the limiting current density, operation ending time should be controlled strictly..

ED is used for the desalination of seawater to produce fresh water. It offers several advantages, such as high water recovery and high desalination ratio [213–215]. However, its applications on the industrial scale have been limited due to restricted choice of IEMs leading to high energy consumption. This is due to the reason that the IEMs used at first were heterogeneous having high area resistance and poor perm-selectivity. It is not economically competitive compared to other desalination technologies, such as reverse osmosis (RO), multistage flash (MSF), and multi-effect distillation (MED). However, with the development of homogeneous membranes, the disadvantages mentioned above have been resolved to a greater extent.

Apart from the IEMs issue, membrane fouling also leads to high energy consumptions and therefore, should be resolved urgently. It is mainly induced by the absorption of organic matter and the precipitation of metallic cations (such as,  $Ca^{2+}$  and  $Mg^{2+}$  ions) inside the solution. To decrease the fouling phenomenon,



**Fig. 15.** Classification of the electrodialysis process.



**Fig. 16.** Representative schematic illustration of a conventional electrodialysis stack.

pretreatment or pre-desalination technologies including nano-filtration, micro-filtration, and ultra-filtration could be introduced prior to the addition of feed solution [216,217]. It is also interesting to find that using some porous membranes to assemble the ED stack instead of the conventional IEMs can reduce the fouling of membrane, since the fouling on porous membrane is easy to be removed [218].

Over the past decade, the progress in ED has specially been prominent. With the developments of optimized IEMs for ED on a pilot-scale, the performances of demineralization and re-concentration (or the production) have been greatly improved. More promising results can be expected by integrating ED and other processes. By introducing external forces such as electric pause, ultra-sonic, magnetic field and micro-wave, the ED performance can be increased to a certain extent. Moreover, an ED stack using specialized IEMs with extraordinary antifouling and desalination properties, will be developed in future for treating organic resources.

### 5.3. Bipolar membrane electrodialysis (BMED)

Bipolar membrane electrodialysis (BMED) is the-state-of-the-art technology for resource recycling, energy conversion, and environmental protection. BMED possesses considerably outstanding

characteristics, which are summarized in three points. Firstly, BMED can supply protons and hydroxide ions with high-efficiency without the need of introducing any other salt ions. This is different from the conventional hydrolysis process and is due to the efficient water splitting in the BPMs. The theoretical energy consumption for electrodialytic water dissociation in BMED is 79.9 kJ/mol, which is much lower than the energy consumption of 198.5 kJ/mol in the electrolysis process. Secondly, there are no oxidation or reduction species, which may produce undesirable products in the BMED process. Thirdly, the BMED process is of space-saving, easier installation, and operation. It can be flexibly coupled with many other technologies to achieve a synergistic technological intensification. For these reasons, substantial efforts have been made to use this new technology (on both laboratory and pilot-plant scales) for chemistry, food processing, biochemical industries, environmental protection in aqueous systems and occasionally in non-aqueous systems.

The largest application of BMED technology is found in the production of inorganic acids and bases from the corresponding salts, such as NaCl, Na<sub>2</sub>CO<sub>3</sub>, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, and Na<sub>3</sub>PO<sub>4</sub> [219–221]. Many attempts have been made to produce caustic soda from inorganic salts to challenge the conventional chlorine/alkaline electrolysis process due to lower, theoretical energy consumption

of the BMED process. However, these attempts are frustrated by high operating cost due to the high price of BPMs and unsatisfactory base quality owing to the insufficient perm-selectivity of the membranes at high ionic concentrations.

Apart from the production of inorganic acids and bases, a number of studies have been conducted to test the feasibility of BMED for the separation of organic acid salt and acidification, such as the conversion of citric acid [222,223], lactic acid [224], gluconic acid [225,226], acetic acid [227,228], lactobionic acid [229], formic acid [230], propionic acid [231], malic acid [232], salicylic acid [233], vitamin C [234], and amino acid [232,235,236]. The feasibility of BMED for organic acid production has been proven in these experiments with acceptable current efficiencies and energy consumptions. However, almost all of these studies were conducted with simulated fermentation broths on a laboratory scale. There are still scarce reports of commercial scale applications of this technology for the production of organic acids. The retarded development of BMED for the production of organic acids on an industrial scale is caused by the high capital cost and unsatisfactory technological stability. High capital cost is ascribed to high price of the commercial bipolar and mono-polar membranes and the shortcomings of the commercial membranes. Hopefully, emerging commercial membranes (such as BPMs discussed in Section 2.5) can render more diversity to available IEMs and help decrease the capital cost of this process. Nevertheless, the inherent advantages of BPMs give a profound support for the perfection of BMED for the production of organic acids. For example, a BMED plant was built in China for the production of succinic acid and had a production capacity of production ability around 600 t/a (as shown in Fig. 17).

#### 5.4. Energy conversion and production

Due to the concerns arising from rapid growth (such as pollution and global warming), new urgency in developing renewable and sustainable energy conversion and production technologies is being realized. Many efforts are expanded on the development of IEMs based energy storage and transformation devices, such as reverse electrodialysis (RED), fuel cells (FC), and redox flow batteries (RFB). These processes have persistently been studied with an expectation to achieve highly efficient energy production and conversion. In this section, the working principles, significant upgrades, and main challenges regarding these techniques will be summarized and commented.

##### 5.4.1. Reverse electrodialysis (RED)

Similar to conventional electrodialysis, RED consists of salt

water compartments, fresh water compartments, IEMs, electrodes and electrode compartments with a suitable redox couple [6,237–239]. As shown in Fig. 18, each fresh water channel lies between two salt water channels, which are separated by a CEM on one side and an AEM on the other. As salt water and fresh water mingle, cations and anions diffuse across IEMs with opposite-charged functional groups in opposite directions towards the two electrodes of a RED apparatus. The ionic diffusion flux generates an electrochemical potential, which is recorded as voltage. Electrodes receive the ions and convert them into an electrical current through an oxidation or reduction reaction [240]. The electrical current generated is captured directly by an external load. The process can be seen as a controlled mixing, where the salt concentration of fresh water is increased while that of the salt water is reduced until equilibrium is reached.

The pioneering work in the field of RED was done by Pattle, who used an apparatus called hydroelectric pile to generate electric power [241]. The adopted membrane (PE mixed with resins and cross-linked with PS) can generate potential difference of around 30 mV with high internal resistance in mimicking sea water and river water. Afterwards, Lacey conducted an investigation on RED and concluded that IEMs should have high perm-selectivity, low area resistance combined with dimensional stability, long service life time and low-cost [242]. Turek used CMX and AMX Neosepta (Tokuyama) normal grade membranes and 0.19 mm spacers to minimize the membrane stack's internal resistance and boundary layers' thickness of the compartments for enhancing the power output [243].

For practical applications, the performance of RED is easily limited by the presence of multi-valent ions in natural seawater and river water sources [244,245]. Therefore, IEMs with high selectivity for monovalent/multivalent ions are very beneficial for RED applications. Guler et al. [246] used a surface modification method to prepare tailor-made MIPMs for RED applications. The coating layer is composed of 2-acrylamido-2-methylpropane sulfonic acid as poly-anions with sulfonic groups and N,N-methylene bis(acrylamide) as the crosslinking agent. This tailor-made membrane yielded relatively high power density.

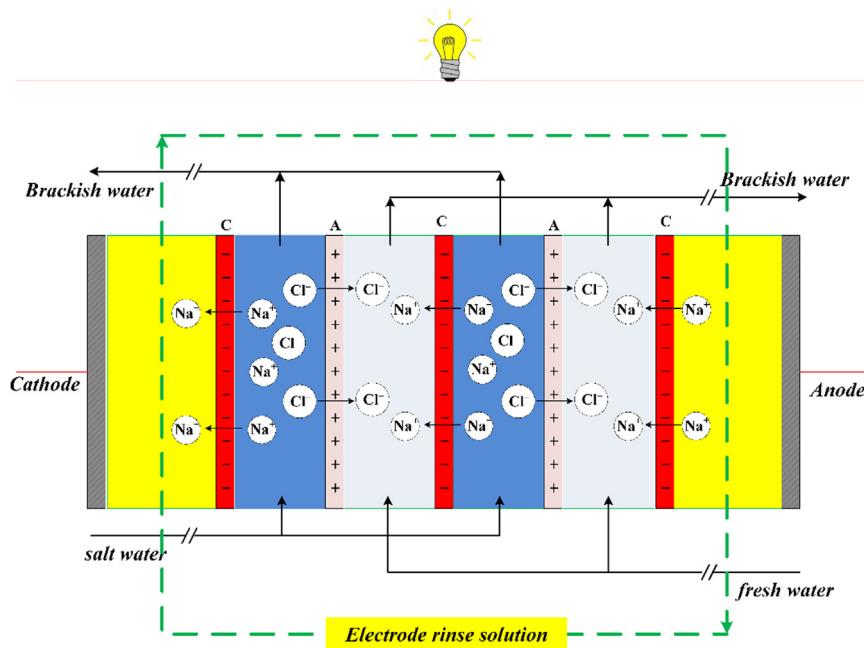
Research has suggested that the power production from the natural water by RED, can be green in nature. IEMs for ED show the trade-off effect between resistance and perm-selectivity. Therefore, exploring novel IEMs with low resistance and high perm-selectivity for RED is of importance and significance.

##### 5.4.2. Redox flow battery (RFB)

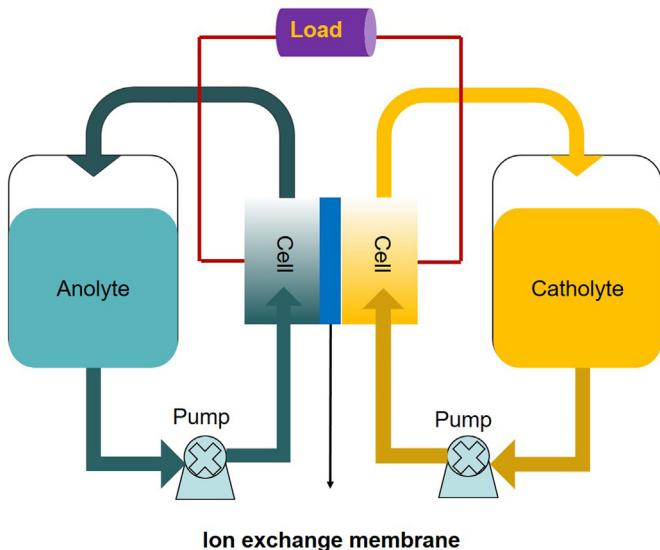
As a promising technology for economical and scalable energy storage, redox flow batteries (RFBs) have received extensive research attention. Over the last decade, various types of RFBs have



**Fig. 17.** Succinic acid production using BMED with production ability around 600 t/a.



**Fig. 18.** The schematic representation of a RED system.

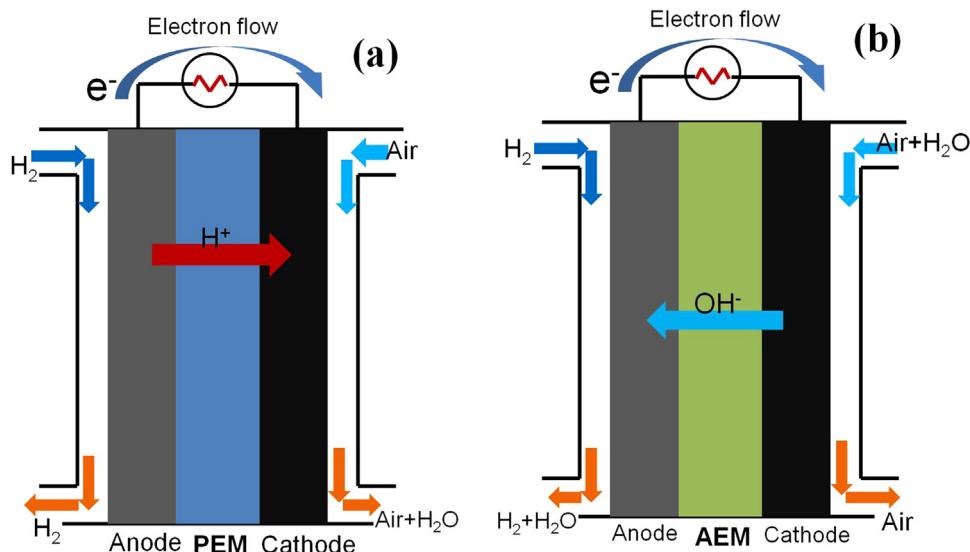


**Fig. 19.** Schematic representation of a redox flow battery system.

emerged, and have been studied intensively. These include all-liquid aqueous flow batteries (all-vanadium RFB (VRFB), iron-chromium RFB, and polysulfide-bromine RFB), flow batteries with metal or gas electrodes (zinc-based RFB, all-iron RFB, and hydrogen-chlorine RFB), and organic flow batteries [247]. In RFBs, energy is generated/stored when the redox species flow through the anode or cathode chambers, which are separated by an IEM. Then, these species undergo electron-transfer reactions at inert electrodes (Fig. 19) [248]. In some types of RFBs, IEMs play a vital role acting as the separator to provide high degree of isolation of electroactive electrolytes and allowing efficient transport of non-electroactive counter ions to balance the charge between anode and cathode chambers. Taking VRFB as an example, perfluoro sulfonic acid (PFSA) CEMs (Nafion® benchmark) are commonly used due to the high proton conductivity, and excellent oxidative

and corrosive stability. However, excessive vanadium crossover, which can cause capacity loss, and extremely high cost (almost 40% of the reaction cell) prevent the industrial consideration of Nafion® for large-scale RFB applications [249,250]. To potentially lower the cost and vanadium crossover of these systems using PFSA benchmarks, alternative aromatic CEMs have been explored in a wide range of studies [251]. Unfortunately, these still experience the critical issue of high vanadium crossover and low oxidative lifetime stability [252]. AEMs having fixed cationic groups are attractive alternatives to CEMs, due to the fact that the electroactive vanadium species in VRFB are positively charged. Additionally, AEMs also offer advantages of high durability in the oxidative environment. The vanadium cations cannot easily penetrate in the membrane, which possibly mitigates the oxidative degradation of the aromatic AEMs [253–255]. According to the basic principle of the CEM-based VRFB, the charge/discharge reaction can be balanced by proton diffusion between the electrode components. For the AEM-based VRFB, the charge can be balanced originating from the shuttling of anions across the IEMs. It should be noted that the anions have intrinsically lower mobility than protons. Hence, the high conductivity and optimization of the conductivity/crossover selectivity ratio are critical in these systems. For most of the reported benzyltrimethylammonium-containing AEMs, conductivity/crossover selective ratios were commonly tuned by either varying the concentrations of fixed charge ions in IEMs [256] or designing IEMs with special structures [257]. A low concentration will induce high ohmic losses and decrease the power density of the cell, while a high concentration will generally cause a high crossover to impact the power output. To alleviate this dilemma, a novel AEM containing ionic knots (zwitterionic groups) has been reported recently [200]. The high concentration of fixed ammonium cations is responsible for the resulting high conductivity, while uniformly dispersed ionic knots in the membrane can maintain low electroactive vanadium species crossover and high chemical stability. The resultant IEMs exhibited a coulombic efficiency of 97.1%, which is higher than that of Nafion® (89.7%, tested under the same conditions)..

To date, most studies on the membrane development for RFBs



**Fig. 20.** Schematic representations of polymer electrolyte membrane fuel cell: (a) proton exchange membrane fuel cell (PEMFC), (b) anion exchange membrane fuel cell (AEMFC).

have focused on basic descriptions of IEM performances, but little attention has been paid on long life-time. Industrial scale RFBs are required to be operated for tens of thousands of cycles. Hence, the technical and practical challenging questions for developing stable IEMs with proven stability over long periods of time necessitate further research.

#### 5.4.3. Fuel cell (FC)

Polymer electrolyte fuel cell (FC) is a fascinating technique, since it has tremendous potential in converting chemical energy derived from a variety of fuels including hydrogen, alcohol, and hydrazine into electricity. The development of FC strongly relays on the advancement of IEMs. In principle, an IEM is sandwiched between the electrodes of FC and selectively conducts protons (for proton exchange membrane fuel cell (PEMFC)); Fig. 20(a) or hydroxide ions (for anion exchange membranes fuel cell (AEMFC)); Fig. 20(b), while preventing the transport of electrons and blocking passage of fuels. The proton exchange membranes (PEMs), conducting protons from anode to cathode, have been extensively studied as PEMFCs offering higher efficiency compared to AEMFC. Moreover, PEMs exhibit high proton conductivity and high thermal and chemical stability, though these have serious challenges associated with fuel cell operating conditions [258,259]. Unfortunately, strong acidic conditions of PEMFC operation require the use of very expensive electro-catalysts for fuel oxidation and hence, affect the long term stability of PEMs [258]. Anhydrous PEMs for high temperature FC was proposed to resolve such challenges, but heat management is a critical factor due to an increase in temperature [260]. Alternatively, AEMs are currently emerging as AEMFC uses cheap catalysts and allows the use of diverse fuels [261]. However, the hydroxide conductivity and alkaline stability are serious challenges regarding the performance of AEMs [262]. In contrast to proton transport in PEMs, anions have low mobility, which restricts the increase of membrane anion conductivity [263]. This section discusses the development and prospects of both PEMFC and AEMFC..

PFSA ionomers are traditionally high performance PEMs and are often used as standard membranes in PEMFC due to their high proton conductivity, and good thermal and mechanical stability as well as high resistance to chemical attack (such as, peroxide degradation) [264–266]. To get rid of poisoning fluorine, studies on cost-effective fluorine free polymers have been investigated for

possible applications in FCs [258,267]. The studies on this system have shown intensive growth over the past decades. The viable strategies within the preparation and design of non-fluorine PEMs have been stated in Sections 2 and 3, and thus, unnecessary details will not be given here regarding this aspect.

Similar to PEMFCs, AEMFCs rely on the performance of AEMs. Many efforts have been expanded to develop high performance AEMs, whereas a few of the developed AEMs have shown satisfactory properties as described in above Section 2.2. In addition to addressing the problems faced by AEMs as separators, searching for suitable ionomers having acceptable stabilities for fabricating compact membrane electrode assemblies (MEAs) is also needed to be solved urgently. This ionomer should exhibit excellent solubility in low-boiling water-soluble solvents such as ethanol or *n*-propanol/2-propanol. The most commonly used quaternary ammonium hydroxide containing polymers have poor solubility in low-boiling water-soluble solvents. In the development of AEMFC, researchers have proposed highly soluble, alkaline stable and high hydroxide conductive ionomers [177,268]. This research area is still in its infancy, and further investigations are needed to develop high performance AEMFC.

These renewable techniques are expected to make great contributions to solving energy crisis, whereas there are still severe challenges regarding the aspects of materials (suitable IEMs) and devices, which prevent their potential pilot-scale applications. It is worth mentioning that, a few IEMs present elegant properties during ex-situ characterizations, while the outcomes obtained are not satisfactory when these IEMs are integrated into afore mentioned devices. In this regard, better understanding towards the in-situ working of IEMs is imperative.

## 6. Summary and perspective

Ion exchange membranes emerging as renewable materials play prominent roles in promoting the development of traditional industry and innovative energy technologies. To date, most of the attention has been focused on exploring promising materials, developing diverse preparation methods, and expanding a wide variety of applications related to ion exchange membranes.

Over the past ten years, such field has significantly bloomed and a large number of achievements have been gained. To date,

there are a tremendous number of ionic polymer candidates available for the preparation of various kinds of ion exchange membranes, including cation exchange membranes, anion exchange membranes, monovalent ion perm-selective membranes, mixed matrix membranes, and bipolar membranes. Although progresses in exploring new ion exchange membranes are prominent, there are still a few challenges, which need to be urgently addressed. For example, the chemical stability of the membranes should be promoted furthermore to ensure the longevity of their lifetime in various applications.

Apart from the intrinsic characteristics of materials, choosing appropriate preparation methods is also of pivotal importance to accomplish desired membrane performances. Currently, a series of techniques such as polymer blending, pore filling, in-situ polymerization and electro-spinning, have shown promise in preserving and occasionally improving the elegant properties of pristine polymers. To date, the studies on the preparation methods are not very detailed and only the feasibility of these methods has been demonstrated. Further exploration and optimization of operating conditions are essential to achieve precise control in structure and composition of improved ion exchange membranes.

Along with the advancements of materials and preparation methods for ion exchange membranes, the corresponding applications have also made rapid progress. Typical applications involving IEMs include diffusion dialysis, electrodialysis, bipolar membrane electrodialysis, reverse electrodialysis, fuel cells, and redox flow batteries. Although some of them have come true or may come true from the viewpoints of industries, their integration of these applications is still scarce and some technical puzzles need to be solved.

Besides, more available ion conducting mechanisms should be proposed after achieving a deeper understanding towards the transport issues within confined space. Porous ion exchange membranes from polymers of intrinsic microporosity and Troger's Base [269] as well as porous fillings such as metal-organic framework, and covalent organic framework also deserve special attention, as these may achieve extremely high separation efficiency and beat the "trade-off" effect in IEMs-based process. Finally, it should be emphasized that materials, preparation methods, and potential applications in the area of ion exchange membranes need to be synergistically explored and taken forward.

## Acknowledgments

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## Nomenclature

<b>ACG</b>	anion conducting group
<b>AEL</b>	anion exchange layer
<b>AEM</b>	anion exchange membrane
<b>AFM</b>	atomic force microscope
<b>ARDD</b>	acid recovery diffusion dialysis
<b>ATRP</b>	atom transfer radical polymerization

<b>BMED</b>	bipolar membrane electrolysis
<b>BPM</b>	bipolar membrane
<b>BPPO</b>	brominated poly(2,6-dimethyl-1,4-phenylene oxide)
<b>BRDD</b>	base recovery diffusion dialysis
<b>CED</b>	conventional electrodialysis
<b>CEM</b>	cation exchange membrane
<b>CEL</b>	cation exchange layer
<b>CGMD</b>	coarse-grained molecular dynamics
<b>CNT</b>	carbon nanotube
<b>CPPO</b>	chloroacetylation PPO
<b>DABCO</b>	1,4-diazabicyclo[2.2.2]octane
<b>DD</b>	diffusion dialysis
<b>ED</b>	electrodialysis
<b>EDI</b>	electro-deionization
<b>EFE</b>	electric field enhanced
<b>EPH</b>	monophenyltriethoxysilane
<b>FC</b>	fuel cell
<b>GMA</b>	glycidyl methacrylate
<b>GO</b>	graphene oxide
<b>IEC</b>	ion exchange capacity
<b>IEM</b>	ion exchange membrane
<b>LBL</b>	layer-by-layer
<b>IL</b>	interfacial layer
<b>MEA</b>	membrane electrode assembly
<b>MED</b>	multi-effect distillation
<b>MIPM</b>	monovalent ion perm-selective membrane
<b>MMM</b>	mixed matrix membrane
<b>MPS</b>	methacryloxypropyl trimethoxy silane
<b>MSF</b>	multistage flash
<b>PAES</b>	poly(arylene ether sulfone)
<b>PAH</b>	poly(allylamine hydrochloride)
<b>PAN</b>	polyaniline
<b>PBI</b>	polybenzimidazole
<b>PE</b>	polyethylene
<b>PEG</b>	polyethylene glycol
<b>PEEK</b>	poly(ether ether ketone)
<b>PEK</b>	poly(ether ketone)
<b>PEI</b>	polyethyleneimine
<b>PES</b>	poly(ether sulfone)
<b>PFSA</b>	perfluoro sulfonic acid
<b>PI</b>	polyimide
<b>PP</b>	polypropylene
<b>PPO</b>	poly(phenyl oxide)
<b>PS</b>	polystyrene
<b>PSS</b>	poly(sodium 4-styrene sulfonate)
<b>PTFE</b>	polytetrafluoroethylene
<b>PVA</b>	polyvinyl alcohol
<b>PVDF</b>	polyvinylidene
<b>Poly(VBC-<i>co</i>-<math>\gamma</math>-MPS)</b>	poly(vinyl benzyl chloride- $\gamma$ -methacryloxypropyl trimethoxy silane)
<b>QPO</b>	quaternized PPO
<b>RED</b>	reverse electrodialysis
<b>RFB</b>	redox flow battery
<b>RO</b>	reverse osmosis
<b>SAD</b>	selected area diffraction
<b>SAXS</b>	small angle X-ray scattering
<b>SED</b>	selective electrodialysis
<b>SPPO</b>	sulfonated poly(2,6-dimethyl-1,4-phenyleneoxide)
<b>TEM</b>	transmission electro microscope
<b>TEOS</b>	tetraethoxysilane
<b>TMA</b>	trimethylamine
<b>TMHDA</b>	N,N,N,N-tetramethyl-1,6-diaminohexane
<b>TPED</b>	two-phase eletrodialysis
<b>U<sub>H</sub><sup>+</sup></b>	proton flux
<b>U<sub>OH</sub><sup>-</sup></b>	hydroxide flux

<b>VBC</b>	vinybenzyl chloride
<b>VRFB</b>	all-vanadium RFB
<b>VTMS</b>	vinyltrimethoxysilane

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