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NEW INVESTIGATIONS IN ION-EXCHANGE MEMBRANES SYNTHESIS AND THEIR MODIFICATION

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.

Keywords: ion exchange, ion-exchange membranes, membrane technology.

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. Quaternary ammonium cations, imidazole cations, and guanidinium cations are generally anchored onto the polymer backbones to obtain AEMs [1, 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. Recently, IEMs have significantly contributed to overcome the problems associated with energy and environment. Diverse electrochemical technologies such as polymer electrolyte membrane fuel cells, redox flow batteries, reverse electrodialysis cells, and water electrolysis 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 [1].

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 [3]. 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 figure 1. We realize a brand-new review to summarize the progresses of IEMs is given urgently. Particularly, with the rapid progress in nanoscience, 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 [1–3].

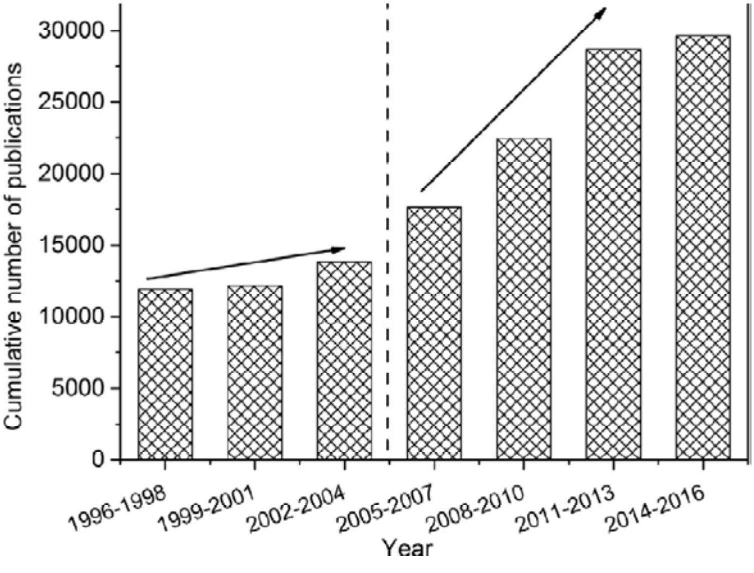

Figure 1 – Chronological advancement of ion exchange membrane in the past 20 years. Source: www.scopus.com; Search settings: ion exchange membrane including articles, conferences, notes, books and review papers; Last accessed: August 2016

Anion exchange membranes (AEMs). AEMs are generally prepared from positively charged polyelectrolytes 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 [4].

AEMs with new cationic head groups. Quaternized ammonium (QA) groups (figure 2a) 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) [1, 5]. 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) (figure 2b), hexamethylenetetramine (figure 2c), N,N,N,N-tetramethyl-1,6-diaminohexane (figure 2d) (TMHDA), and N,N,N,N-tetramethyl-1,2-diaminoethylene etc. [6]. 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.

Nitrogen containing conjugated molecules are potential ACGs for AEMs. Guanidinium cations (figure 2e) were firstly investigated as ACGs for AEMs by Zhang and co-works. 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) (figure 2f) 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. More recently, extensive research efforts have been devoted to the development of imidazolium based AEMs (figure 2g) 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. Afterwards, Price and co-works 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 and reversible deprotonation

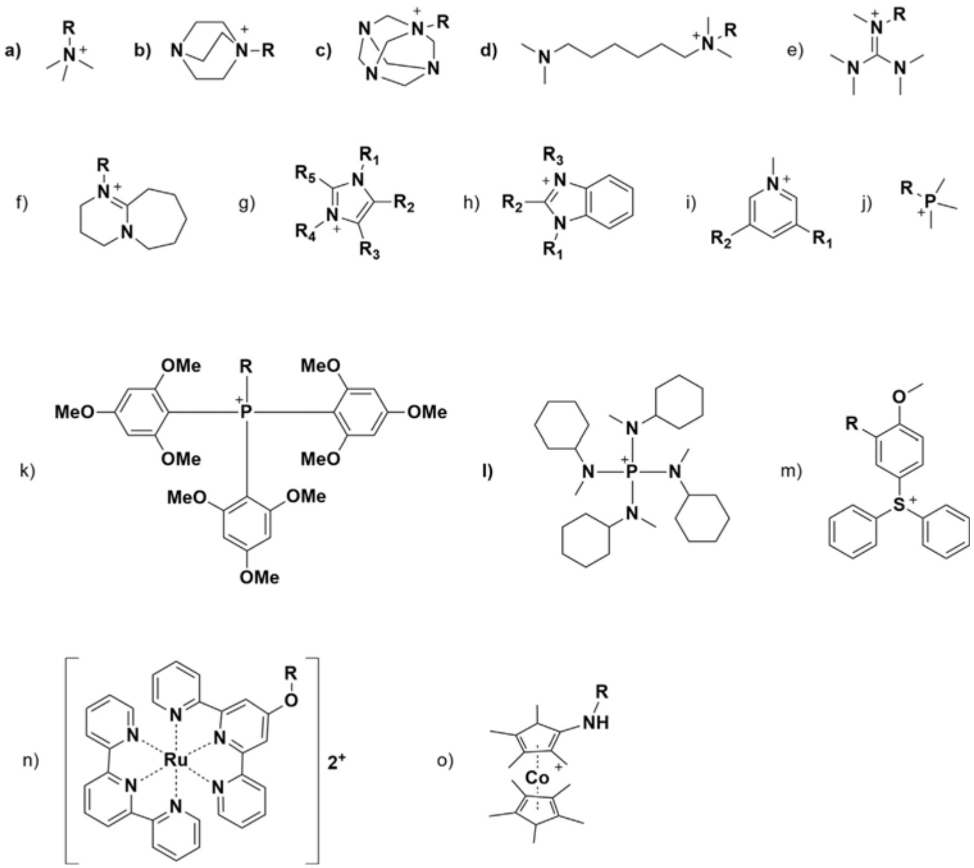

Figure 2 – Commonly encountered anion conducting groups for anion exchange membrane

reactions, is the key factor that decides the stability of imidazolium cations. On the other hand, Yan and co-workers 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 (figure 2h) hold great promise to serve as ACGs for AEMs. Holdcroft and co-workers synthesized benzimidazolium based AEMs by methylation of PBI. By introducing a bulky tirmethylphenyl ring to the C2 position of benzimidazole, stable main chain functionalized type AEMs were successfully synthesized. 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 [7, 8].

Pyridine-based AEMs (figure 2i) were synthesized by our group and employed in the separation of various anions. Improved hydrophilicity and anion permeability were observed for pyridinebased 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 (figure 2j) or triphenylphosphine. However, this type of AEMs have proved to be unstable in alkaline media because of severe nucleophilic attack by hydroxide ions. Yan and co-workers [9–12] found that by introducing three electro-donating methoxyl groups into each phenyl ring of triphenylphosphine (figure 2k), cation conductivity and alkaline tolerance of phosphonium based AEMs could be greatly enhanced. This can be ascribed to both steric hindrance and electro-donating effects of methoxyl groups. Another type of phosphonium cation with more complicated structure was synthesized and investigated by Coates and co-works (figure 2l). 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 (figure 2m) act as ACGs for AEMs. Yan and coworkers [11] synthesized the first base stable sulfoniumbased AEM by introducing one electro-donating methoxyl group to the phenyl ring connected to sulfonium cations. Hickner and co-workers [13, 14] prepared metal-cation functionalized AEMs by copolymerization and cross-linking of dicyclopentadiene and norbornene monomers bearing a water-soluble bis(terpyridine)ruthenium (II) complex (figure 2n). 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 coworkers reported permethyl cobaltocenium based AEMs (figure 2o), which have reduced positive charges on the metal center. This cobalt based AEM exhibited excellent stability.

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, acid recovery in hydrometallurgy and removal of specific ions from liquid waste. 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. The strategies used for regulating such factors have been reported in the literature. Some of these strategies are as follows [15].

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 crosslinked 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 (figure 3). 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 [16, 17].

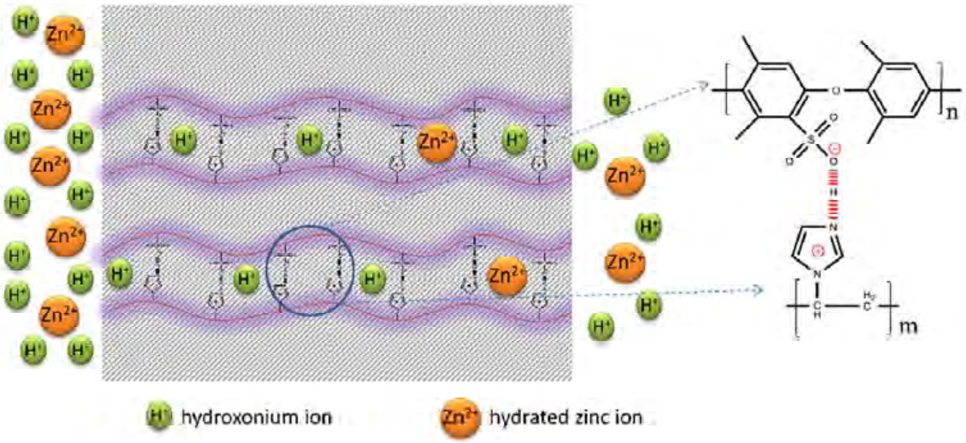

Figure 3 – Constructing H^+ transfer channels through the formation of acid-base pairs

Although cross-linking is especially fascinating in preparing MIPMs, high electrical resistance caused by the cross-linking is an inevitable issue. To decrease the detrimental influence of cross-linking, conducting layers are introduced onto the MIPM surface. Gohil and co-workers 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 electro-dialysis operation.

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. [18] modified a Nafions 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 layerby-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. Mulyati et al. [19] 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. [20] prepared monovalent cation perm-selective membranes by surface polymerization of 4-vinypyridine monomers initiated by the generated radicals during the oxygen plasma treatment. The resultant membrane showed high monovalent cation perm-selectivity and low membrane resistance.

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. Nagarale et al. [21] investigated a series of CEMs having different functional groups including sulfonic acid, phosphonic acid, and carboxylic acid 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. [22] 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.

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. 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 [23]. 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.

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. Figure 4a shows a schematic illustration of the structure and function of BPMs. When a potential (40.83 V) is applied across the mem-brane, a very large electric field (108 V/m) is generated in the IL. The water mo-lecules residing in the IL become sufficiently polarized and hence, get dissociated. Figure 4b 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. 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 [1, 24].

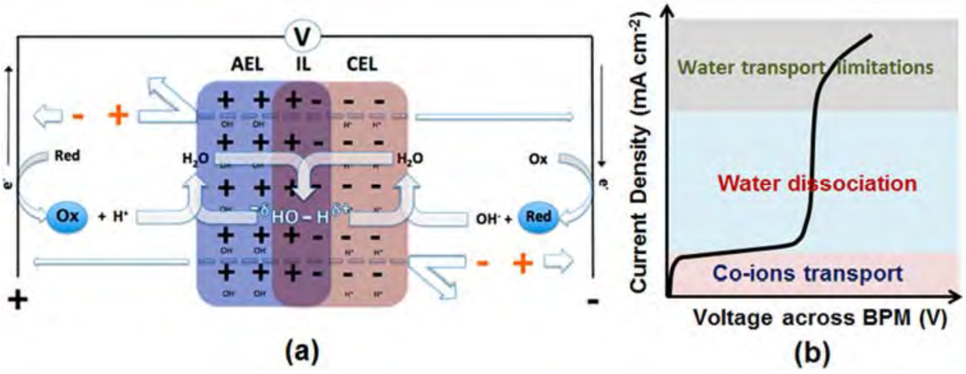

Figure 4 – Schematic illustrations of (a) the structure and function of a BPM; (b) a typical I-V curve of a BPM in a salt solution

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. 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 to that of the water dissociation reaction constant pKa¼7, e.g. amino groups (primary, secondary or tertiary amine), and pyridines could be incorporated into the IL. Our previous work have demonstrated the catalytic activities of hydrophilic macromolecules, including polyethylene glycol (PEG), PVA, and hyper-branched polymers. Additionally, inorganic substances, such as GO, and heavy metal ions complexes could also been incorporated into IL for enhancing the water dissociation [25].

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.

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 [26] 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 effi- ciency 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.

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Резюме

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ИОНАЛМАСТЫРҒЫШ МЕМБРАНАЛАРДЫҢ ЖАҢА ЗЕРТТЕУЛЕР СИНТЕЗДЕУ ЖӘНЕ МОДИФИКАЦИЯЛАУ

Ионалмастырғыш мембраналар әртүрлі қолданыстарда үлкен әлеуетке ие және энергетика мен қоршаған ортаға қатысты мәселелерде үлкен рөл атқарады. Соңғы онжылдықта ионалмастырғыш мембраналардың дамуы академиялық және өндірістік құндылықтары арқасында материал, дайындау және қолдану тұрғысынан зерттеушілердің аса назарын аударды. Бұл шолу мақаласында негізгі стратегияларды түсінуді және қойылған мақсаттарға қол жеткізуді қамтамасыз ете отырып, ионалмастырғыш мембраналардың синтезі мен түрленулері туралы жаңа зерттеулерге арналған әртүрлі жұмыстардағы жетістіктер талданып қорытылған. Дайындаудың оңтайландырылған әдістері мембраналардың сапасын жақсарту үшін өте маңызды. Ионалмастырғыш материалдар осы шолу мақаласында жинақталған синтезге және түрленуге жаңа зерттеулерді енгізеді.

Түйін сөздер: ион алмасу, ион алмасу мембраналар, мембраналық технология.

Резюме

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НОВЫЕ ИССЛЕДОВАНИЯ В СИНТЕЗЕ И МОДИФИКАЦИИ ИОНООБМЕННЫХ МЕМБРАН

Ионообменные мембраны обладают большим потенциалом в различных применениях и играют огромную роль в вопросах, касающихся энергетики и окружающей среды. За последние десятилетия развитие ионообменных мембран привлекло большое внимание исследователей с точки зрения материалов, подготовки и приложений, благодаря их академических и промышленных ценностей. В этом обзоре обобщены достижения в различных работах, посвященных новым исследованиям в синтезе и модификации ионообменных мембран, обеспечивая понимание основных стратегий и достижения поставленных задач. Оптимизированные методы подготовки имеют решающее значение для повышения качества мембран. Ионообменные материалы предполагают новые исследования в синтезе и модификации, которые обобщены в этом обзоре.

Ключевые слова: ионный обмен, ионообменные мембраны, мембранная технология.