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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, andazole 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

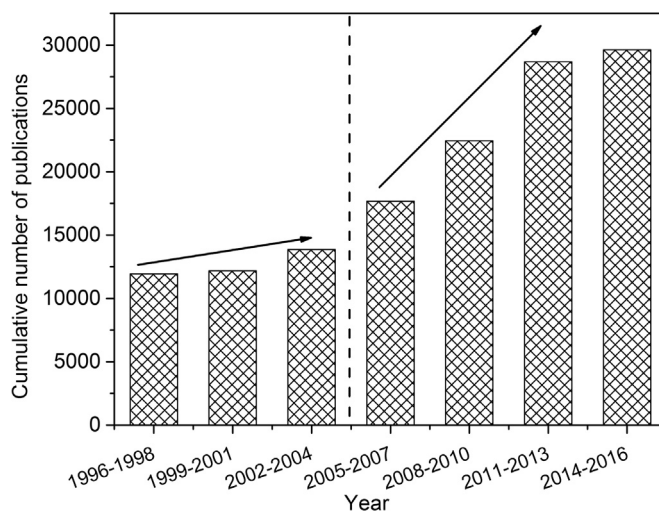


Fig. 1. Chronological advancement of ion exchange membrane in the past 20 years. Source: [www.scopus.com](http://www.scopus.com); Search settings: ion exchange membrane including articles, conferences, notes, books and review papers; Last accessed: August 2016.

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