Selectivity of ion exchange membranes: A review

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ABSTRACT

Ion exchange membranes (IEMs) have been established as a key component in industrial water desalination and electrolysis processes. Thus, nowadays, they are being studied and developed for application in new energy conversion and storage systems as well as efficient desalination and wastewater treatment processes. These processes include redox flow batteries, reverse electrodialysis, membrane capacitive deionization, microbial fuel cells, and ion exchange membrane bioreactors. Ion permselectivity between counter- and co-ions, the most essential property in IEMs, makes these processes possible and/or efficient. Additionally, ion selectivity between different counter-ions is required for these novel processes to be efficient. This review aims to provide a comprehensive overview of ion exchange membrane permselectivity by summarizing the developments in this field over the past decade. Membrane microstructure and possible mechanisms for ion transport in the membrane phase are discussed with respect to permselectivity, along with the influence of current density and related membrane-solution boundary conditions. A selectivity order for the transport of common anions through conventional anion exchange membranes (AEMs) is generalized, the same is done for cation transport through conventional cation exchange membranes (CEMs). Two types of experimental methods for the determination of ion permselectivity: electrodialysis and the membrane potential method, are summarized. Finally, relevant membrane preparation methods and surface modification of IEMs reported over the past decade are classified and discussed. In summary, we conclude that synthetic methods have evolved rapidly; however, development of fundamental knowledge on the many complex phenomena occurring in the adaptive membrane bulk and solution-interface environments is not sufficiently established. Thus, much effort is required to combine experimental, theoretical, and simulation data for a more comprehensive and coherent understanding of these phenomena.

1. Introduction

1.1. Established and emerging applications of IEMs

IEMs are an important class of dense polymeric membranes that bear fixed charges in the polymer matrix. These membranes can selectively allow the passage of oppositely charged ions (counter-ions), while obstructing similarly charged ions (co-ions). IEM permselectivity for counter-ions was first elucidated by Donnan [1]; thus, the mechanism is referred to as the Donnan effect or Donnan exclusion (towards co-ions). Due to this ion permselectivity, several industrial processes based on IEMs, including electrodialysis (ED), diffusion dialysis (DD), and electrolysis, have been established. Apart from ED and DD, IEMs have also been widely studied as a key component in flow batteries as well as some emerging new applications including membrane capacitive deionization (MCDI), reverse electrodialysis (RED), microbial fuel cells (MFCs), and ion exchange membrane bioreactors

(IEMBs). IEMs with low fixed charge density are also studied as chlorine-tolerant membranes in reverse osmosis (RO) for sea water desalination. As summarized in Table 1, these different processes employ different driving forces and aim to help address increasing global concern on energy shortage [2,3], environmental issues, and depletion of drinking water sources.

1.2. Requirements for better ion selectivity

With the growing number of IEM applications, permselectivity between counter- and co-ions as well as counter-ions of different (monovalent and multivalent, *e.g.* Li^+ and Mg^{2+} [22]) or equal (*e.g.* NO_3^- and Cl^-) valences, is desirable. Thus, as illustrated in Table 1, processes such as flow batteries, diffusion dialysis (DD), microbial fuel cells (MFCs), and ion exchange membrane bioreactors (IEMBs) all require high membrane permselectivity between counter-ions of different valences. In flow batteries, the essential function of an IEM is to isolate

Table 1
Different processes that employ ion exchange membranes (IEMs).

Process	Driving force for ion transport	Ion selectivity	Application	Refs.
ED*	∇U*	Co- and counter-ions	Water desalination, NaCl production	[4–8]
Flow batteries	$\nabla \mu$* (discharge) ∇U (charge)	Na^+/H^+ and other ions	Energy storage and conversion	[9]
DD*	∇c*	H^+ and OH^- leakage	Recovery of acids	[10]
MCDI*	∇U	Co- and counter-ions	Water desalination	[11,12]
RED*	∇c	Co- and counter-ions	Energy conversion	[13–16]
RO*	∇c, ∇P*	Retention of salt	Water desalination	[17,18]
MFC*	$\nabla \mu$	H^+ and Na^+	Waste biomass treatment, energy conversion	[19,20]
IEMB*	$\nabla \mu$	Co- and counter-ions, different counter-ions	Water treatment	[21]

ED, electrodialysis; DD, diffusion dialysis; MCDI, membrane capacitive deionization; RED, reverse electrodialysis; RO, reverse osmosis; MFC, microbial fuel cells; IEMB, ion exchange membrane bioreactor.
∇U, electrical potential gradient; $\nabla \mu$, chemical potential gradient; ∇c, concentration gradient; ∇P, pressure gradient.

Table 2
Ion selectivity requirements in redox flow batteries [9].

Battery Type	Anolyte	Catholyte	Charge carrier	Membrane	Permselectivity
Polysulfide bromine	$Br_3^-/3Br^-$	S_4^{2-}/S_2^{2-}	Na^+	CEM*	Na^+ and anions
All vanadium	VO_2^+/VO^{2+}	V^{2+}/V^{3+}	H^+	CEM, AEM*	H^+ and V (II–V)
Vanadium bromine	$ClBr^{2-}/Cl^-$, $2Br^-$	V^{2+}/V^{3+}	H^+	CEM	H^+ and V (II, III)
Chromium bromine	Fe^{2+}/Fe^{3+}	Cr^{2+}/Cr^{3+}	H^+	CEM, AEM	H^+ and metal cations
Zinc cerium (non-aqueous)	Ce^{3+}/Ce^{4+}	Zn/Zn^{2+}	H^+	CEM	H^+ and metal cations

CEM, cation exchange membrane; AEM, anion exchange membrane.

the ions of redox couples that are involved in electrode reactions to prevent self-discharge, while allowing the transfer of specific ions (charge carriers) across the membrane at a high rate to complete the electric circuit. The permselectivity of IEMs between redox-active ions and charge carriers determines the coulombic efficiency and ultimately, the energy efficiency of a flow battery. Table 2 lists the different redox-active ions (anolytes and catholytes), charge carriers, and IEMs used in several types of flow batteries. In some cases, for example polysulfide bromine batteries with a cation exchange membrane (CEM), the sole permselectivity required is the separation between counter- and co-ions. However, more often, permselectivity between the metal cations and H^+ ions is desirable. The special "H^+ leakage" through anion exchange membranes (AEMs) bearing fixed positive charges is utilized in all vanadium [23] and chromium bromine batteries and leads to very high coulombic efficiency.

For application of IEMs in IEMBs and MFCs, high permselectivity between the counter-ions is crucial for system efficiency. In the case of IEMBs, the selective transport of toxic oxyanions (ClO_4^-, NO_3^-, BrO_3^-) over other multivalent anions (SO_4^{2-}, HPO_4^{2-}) under Donnan dialysis conditions is desirable to efficiently treat drinking water polluted with these monovalent anions [24]. Recent studies employing commercial monovalent anion selective membrane have exhibited the best performance in terms of selective removal of monovalent anions to the recommended safety levels [21]. Although normal AEMs have larger fluxes of toxic oxyanions (ClO_4^-, NO_3^-, BrO_3^-), the monovalent anion selective membrane still displays better efficiency for SO_4^{2-} and HPO_4^{2-} fluxes that are almost two orders of magnitude lower than those in normal AEMs [21]. However, the high price of monovalent anion selective membranes is a hurdle for the application of this technology. In microbial electrochemical systems such as MFC, selective H^+ transport in the presence of Na^+ with a substantially higher concentration is an even greater challenge [20].

As implied by the "H^+ leakage" of AEMs for flow battery application, the selective transport of H^+ and OH^- ions through IEMs is very important for several technical applications. In DD for the recovery of acids from metal finishing solutions, AEMs with high H^+/metal cation selectivity are desirable [10], while AEMs and CEMs with high H^+ and OH^- retention, respectively, are preferred in electrochemical water splitting with bipolar membranes [25,26].

1.3. Past research motivations

In the past, the practical motivation to study tuned IEM permselectivity was the difficult task to slow down the OH^- transport through the CEM in the electrolysis of NaCl solution to produce Cl_2, NaOH, and H_2 [27]. To date, this chlor-alkali process is still the most relevant industrial application for IEMs. The challenge was tackled with a perfluorosulfonic acid-type CEM bearing a surface layer of perfluorocarboxylic acid groups facing the cathode. This perfluorocarboxylic surface layer has lower water contents compared with its sulfonate analog, and can slow down OH^- transport towards the anode so that Na^+ ions carry most of the current [28,29]. Another motivation was originally to produce table salt (NaCl) in Japan by ED of sea water comprising multivalent Mg^{2+} and Ca^{2+} ions [5,6]. These CEMs require higher transport affinity towards Na^+ than Mg^{2+} and Ca^{2+}, not an intrinsic property of traditional CEMs. Moreover, the AEMs should ideally be more permeable to Cl^- over other anions (SO_4^{2-}). Sata et al. investigated IEM modification to achieve such monovalent ion selectivity and studied the resultant ED performance. These experimental works are summarized in two reviews on AEMs [6] and CEMs [5]. A recent review summarizes the patents for the preparation methods of CEMs with monovalent cation selectivity [30]. This topic of ion permselectivity is also briefly discussed in a very recent review on IEMs by Ran et al. [31]. Xu et al. [32] published a monograph on monovalent cation permselective membranes, with a focus on the traditional and emerging preparation/modification methods for these membranes. They also proposed a ionic flux – permselectivity trade-off plot for several couples of monovalent/bivalent cations [32].

Sata et al. demonstrated that in ED, counter-ions of different valences can be kinetically separated by a membrane surface layer bearing the same charge as the counter-ions [33]. Thus, commercialized monovalent ion selective IEMs could also find further niche applications such as the demineralization of whey [34] and electro-acidification of milk *via* bipolar membrane ED to produce high-purity bovine milk casein isolates [35]. However, the high fabrication cost of such IEMs impedes their utilization in wider applications such as flow batteries and IEMBs. Even NaCl production from sea water ED in Japan is heavily subsidized by the government [36]. Therefore, there is a need to advance the development of IEMs with tuned ion selectivity, including further understanding of ion transport in the IEM system and