

Advancing ion-exchange membranes to ion-selective membranes: principles, status, and opportunities

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HIGHLIGHTS

- IEM ion/ion selectivities of charge, valence, & specific ion are critically assessed.
- Ion/molecule selectivities of ion/solvent and ion/uncharged solute are reviewed.
- Approaches to advance the selectivities through sorption and migration are analyzed.
- The permeability-selectivity tradeoff appears to be pervasive.
- Ion/molecule selectivities are comparatively underdeveloped and poorly understood.

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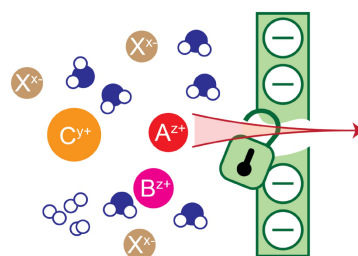
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ABSTRACT

Ion-exchange membranes (IEMs) are utilized in numerous established, emergent, and emerging applications for water, energy, and the environment. This article reviews the five different types of IEM selectivity, namely charge, valence, specific ion, ion/solvent, and ion/uncharged solute selectivities. Technological pathways to advance the selectivities through the sorption and migration mechanisms of transport in IEM are critically analyzed. Because of the underlying principles governing transport, efforts to enhance selectivity by tuning the membrane structural and chemical properties are almost always accompanied by a concomitant decline in permeability of the desired ion. Suppressing the undesired crossover of solvent and neutral species is crucial to realize the practical implementation of several technologies, including bioelectrochemical systems, hypersaline electrodesalination, fuel cells, and redox flow batteries, but the ion/solvent and ion/uncharged solute selectivities are relatively understudied, compared to the ion/ion selectivities. Deepening fundamental understanding of the transport phenomena, specifically the factors underpinning structure-property-performance relationships, will be vital to guide the informed development of more selective IEMs. Innovations in material and membrane design offer opportunities to utilize ion discrimination mechanisms that are radically different from conventional IEMs and potentially depart from the putative permeability-selectivity tradeoff. Advancements in IEM selectivity can contribute to meeting the aqueous separation needs of water, energy, and environmental challenges.

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1 Introduction

The advancement in selectivity of existing separation techniques and the development of new technologies with improved selectivity have been identified as critical aqueous separation needs for water, energy, and the

environment (Clark et al., 2016; Tirrell et al., 2017; National Academies of Sciences and Medicine, 2019). For example, nitrogen and phosphorus are macronutrients essential for food production. The manufacturing and extraction of N and P are very energy-intensive: 19.3 kWh/kg-N, amounting to $\approx 2\%$ of global power consumption, and 2.1 kWh/kg-P (Erisman et al., 2008; Elser and Bennett, 2011). At the same time, these nutrients are pollutants in wastewaters. The development of selective technologies to recover NO_3^- , NH_4^+ , and $\text{H}_2\text{PO}_4^{x-3}$ from complex streams containing other ionic species will

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contribute to the realization of a more sustainable circular nutrient economy (Li et al., 2015; Ye et al., 2020; McCartney et al., 2021). Likewise, the targeted removal of trace contaminants, e.g., Pb^{2+} , Hg^{2+} , Cd^{2+} , Cr^{2+} , F^- , H_2AsO_4^- , H_2BO_3^- , and SeO_4^{2-} from background ions are pivotal for water security (Zhang et al., 2009; Clark et al., 2016; Tirrell et al., 2017; Wang et al., 2019; Grzegorzec et al., 2020). Similar selectivity challenges exist in energy applications. Critical materials are essential to economic prosperity and the transition to a clean energy economy (Chu, 2011; Office of Energy Efficiency and Renewable Energy and Advanced Manufacturing Office, 2020). Innovations in tailored separation selectivity for Li^+ can enable the economic recovery of lithium, a critical mineral for energy security, from unconventional streams, such as geothermal brines (The White House, 2018; Warren, 2021). The separation of individual rare earth elements from one another is technically difficult and very energy-demanding because of chemical similarities resulting from their proximity on the periodic table. As such, the development of separation technologies with improved efficiencies has been identified as one of the strategic responses for securing rare earth supply chains (Office of Energy Efficiency and Renewable Energy and Advanced Manufacturing Office, 2020).

Ion-exchange membranes, IEMs (also termed polymer electrolyte membranes), are polymeric films with charged ionic functional groups that allow the transport of oppositely-charged species (counterions), while retaining like-charged ions (co-ions) (Sata, 2004; Strathmann, 2004). IEMs have been successfully employed in water, environmental, energy, and chemical production applications, such as electrodialysis desalination, fuel cells, and the chloralkali process (Sata, 2004; Strathmann, 2004; Ran et al., 2017). Beyond the primary function of *charge* selectivity (i.e., differentiating between counter- and co-ions), IEMs can potentially be employed for other selective separations. Discrimination between like-charged ions with different *valences* will, for example, enable IEMs to separate and recover Li^+ from Mg^{2+} in lithium-rich brines (Nie et al., 2017b). Further advancing IEM selectivity to discern between different ions with the same valence will enable *specific ion* separations. An example would be the segregation of Co^{2+} and Ni^{2+} from each other for battery recycling (Huang et al., 2019; Alvia-Hein et al., 2021). In IEM processes, solvent and neutral solutes can transport across the membrane, commonly termed crossover. Several applications necessitate IEMs to be selective for the transport of ions over solvent, with a notable example being direct methanol fuel cells, in which the crossover of water is a principal limitation constraining performance (Kreuer, 2014). Some IEM processes require the suppression of uncharged species crossover in order to be feasible. For instance, in water electrolyzers, dissolved H_2 transported across the membrane mixes with the evolved $\text{O}_{2(g)}$, posing

explosion hazards (Collong and Kouta, 2015; Kim et al., 2021b). Therefore, advancing the function from just ion *exchange* to ion *selective* separations would improve the cost-effectiveness and energy-efficiency of current IEM applications and expand their utility to meet emerging separation needs. To this end, several recent articles offer insightful reviews on the selectivity of ion-exchange membranes (Kreuer, 2014; Luo et al., 2018; Epsztein et al., 2020; Sujanani et al., 2020; Tang and Bruening, 2020; DuChanois et al., 2021; Kreuer and Münchinger, 2021; Wang et al., 2022b). However, reviews that encompass all the different types of selectivity listed above are presently lacking in literature, with ion/solvent and ion/uncharged solute selectivities, in particular, being frequently overlooked.

In this review, we critically assess the charge, valence, specific ion, ion/solvent, and ion/uncharged solute selectivities of ion-exchange membranes. First, the fundamentals of ion transport in IEM are presented, to provide the theoretical framework based on sorption and migration for understanding the underlying principles governing the different separation selectivities. The implications of the tradeoff between permeability and selectivity are then discussed. Next, we examine the roles of sorption and migration in the five different types of selectivities and summarize the current progress. In particular, permeability-selectivity tradeoffs are highlighted and technological pathways for advancement are critically analyzed. Last, we share our perspectives on the outlook of ion-selective membranes. This review seeks to stimulate research interest and serve as a starting point for the informed development of more selective ion separation membranes.

2 Membranes for ion transport

This section introduces the sorption-migration framework for ion transport (Sata et al., 2002; Sata, 2004; Strathmann, 2004; Luo et al., 2020), which will be used as the basis for subsequent analyses of the different IEM selectivities. The key governing transport equations are presented and the roles of sorption and migration selectivities in the overall separation selectivity between two species are highlighted. We then point out the seemingly ubiquitous tradeoff between selectivity and permeability, and broadly discuss the practical implications.

2.1 Sorption-migration of ion transport

Ion transport across IEMs can be described by the “sorption-migration” mechanisms, which are analogous to solution-diffusion for gas separation and reverse osmosis membranes (Wijmans and Baker, 1995; Paul, 2004; Kamcev et al., 2017). Ions sorb or partition into the

membrane (parallel to “solution”) and subsequently migrate across the membrane under an electrochemical potential gradient (corresponding to “diffusion”) (Sata, 2004; Strathmann, 2004; Fan and Yip, 2019), as depicted in Fig. 1(a)). The sorption of ions into the membrane matrix is governed by the thermodynamic equilibrium of the electrochemical potential between the bulk solution and membrane matrix, and is determined by the electrostatic potential difference across the solution-membrane interface, termed the Donnan potential, $\Delta\varphi_D$ (Figs. 1(b) and 1(c)) (Sata, 2004; Strathmann, 2004; Strathmann et al., 2013). The sorption coefficient, K , is defined as the concentration ratio of ion i in the IEM relative to bulk-phase solution and can be described by Eq. (1) (Fan and Yip, 2019):

$$K_i \equiv \frac{c_i^m}{c_i^s} = \frac{f_w \gamma_i^s}{\gamma_i^m} \exp\left(-\frac{z_i F}{RT} \Delta\varphi_D\right), \quad (1)$$

where c is ion concentration, γ is activity coefficient, f_w is water volume fraction in the membrane matrix, z is ion valence, F is the Faraday constant, R is the gas constant, T is absolute temperature, and superscripts m and s denote membrane and bulk solution phases, respectively. Here, c_i^m is ion concentration in the hydrated membrane volume (dividing c_i^m by f_w yields ion concentration in solution phase of the membrane matrix; discussions on the rationale for using solution volume or polymer and solution volume for ion concentration can be found in literature) (Kitto and Kamcev, 2022).

Additionally, electroneutrality within the membrane

needs to be preserved (Eq. (2)):

$$\sum z_{ct} c_{ct}^m + \sum z_{co} c_{co}^m + z_{fix} c_{fix}^m = 0, \quad (2)$$

where z_{fix} and c_{fix}^m are valence and concentration of the membrane fixed charges, respectively, and subscripts ct and co indicate counter- and co-ions. All ionic species (i.e., $z \neq 0$) experience the same nonspecific $\Delta\varphi_D$. Therefore, interfacial ion distribution in the IEM is governed by charge balance and the Donnan potential (Eqs. (2) and (1), respectively), with $\Delta\varphi_D^1$ and $\Delta\varphi_D^2$ dictating ion concentrations at the upstream and downstream solution-membrane interfaces, respectively (superscripts 1 and 2), as depicted in Fig. 1(c)).

Ion flux, J , quantifies permeation across the membrane. The extended Nernst-Planck equation, modified to account for γ , can be used to describe J (Fig. 1(d)) (Tanaka, 2015; Luo et al., 2018):

$$J_i = -D_i^m c_i^m \frac{d \ln(\gamma_i^m c_i^m)}{dx} - z_i e u_i^m c_i^m \frac{d\varphi^m}{dx} + v_w c_i^m, \quad (3)$$

where D^m and u^m are diffusivity and absolute mobility of the ion within the IEM, φ^m is the membrane electrostatic potential, v_w is the velocity of water in the membrane, and e is the elementary charge. The first, second, and third terms of the expression represent Fickian diffusion of ions down an activity gradient, migration of charged species under an electric field (electromigration), and convective (or, more correctly, advective) transport due to fluid flow, respectively. Therefore, Eq. (3) can be termed the convection-diffusion-electromigration equation.

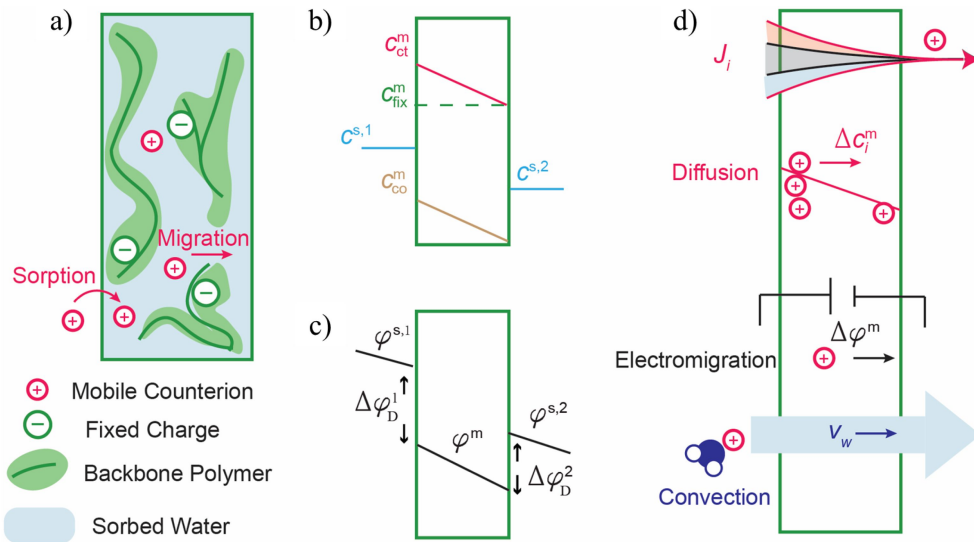


Fig. 1 (a) Schematic illustrating the sorption-migration transport of mobile counterions (co-ions not shown) in a water-swollen cation exchange membrane. (b) Representative schematic of membrane counterion concentration, c_{ct}^m , co-ion concentration, c_{co}^m , fixed charge density, c_{fix}^m , and bulk concentrations, c^s , of two adjacent solutions (denoted by superscripts 1 and 2). (c) Representative schematic of electric potentials: φ^m and φ^s denote membrane and bulk solution potentials, respectively, and $\Delta\varphi_D$ represents the Donnan potentials at solution-membrane interfaces. (d) Schematic illustrating the three transport mechanisms in IEMs, namely diffusion (driven by concentration difference, Δc^m), electromigration (driven by electric potential, $\Delta\varphi^m$), and convection (driven by velocity of transmembrane solvent flow, v_w). Summing the three terms yields the net flux across the membrane, J_i .

The electromigration term can be expressed using D in place of u , as the two terms are linked by the Einstein relation, $u_i = D_i/(k_B T)$ (Bard and Faulkner, 2001; Robinson and Stokes, 2002). However, the mechanism of electromigration transport is fundamentally different from diffusion, and representing the term using diffusion coefficient can cause unnecessary confusion. Further, the product of absolute mobility, valency, and elementary charge, $|z_i|eu_i^m$, is the ion electrical mobility. Hence, the electromigration term can be more intuitively expressed using the absolute mobility, where the influences of ion valence (both integer value and sign) are also explicitly represented in Eq. (3). In this review, u_{ci}^m is considered to be the weighted average of all counterions in the membrane, i.e., mobile/free and condensed/associated (Kamcev et al., 2018a; Münchinger and Kreuer, 2019; Luo et al., 2020; Kitto and Kamcev, 2022).

Transmembrane water flux (driven by osmotic or hydrostatic pressure difference) produces ion advection (third term of Eq. (3)). However, this term is sometimes left out of ion transport equations (Helfferich, 1995; Bard and Faulkner, 2001; Sata, 2004; Berezina et al., 2008). At the same time, the permeating ions drag hydrating water molecules along, a phenomenon termed electro-osmosis (Spiegler, 1958). The intertwined transport of ionic species and water molecules can have non-negligible impacts on selectivity and separation performance. The issue will be revisited in later discussions. Ion concentration polarizations arising from inevitable mass transfer limitations at the solution-membrane interfaces affect the transport of ions, but are not incorporated into the equations presented here to simplify the analysis. Readers are directed to literature for detailed discussion on the impact of ion concentration polarization on selectivity (Rubinstein, 1990; Zabolotsky et al., 2002; Kim et al., 2012; abu-Rjal et al., 2014; Tang and Bruening, 2020).

2.2 Ion selectivity

Overall ion transport of sorption and migration are, therefore, governed by Eqs. (1) and (3), respectively, and constrained by electroneutrality (Eq. (2)). Flux selectivity between two species, i and j , with i being the desired species, can be expressed by the ratio J_i/J_j : unity would signify equal fluxes, whereas ratios greater and lesser than 1 would indicate proportionally higher fluxes of i and j , respectively. However, a crucial shortcoming of J_i/J_j as a selectivity metric is that the relative prevalence of i and j in the bulk solution phases are not factored into the ratio. This inadequacy is not apparent when the two ions are at the same c^s (such as counter- and co-ions in 1:1 electrolytes or Na^+ and Li^+ at equimolar concentrations). However, when one is the minority species among the other predominant ion, say i and j , respectively, simply taking the flux ratio will almost always yield J_i/J_j

< 1 because of the considerably greater presence of species j , even though the fluxes may be enriching for i compared to the bulk solutions, i.e., $J_i/J_j > c_i^s/c_j^s$. Therefore, the actual ability of the membrane to selectively discern between different ions may be confounded. The commonly used metric of transport number (t , defined as fraction of ionic current carried by the species of interest relative to the total ionic current) (Strathmann, 2004; Luo et al., 2018), though useful in the appropriate context, is generally afflicted by the same issue of being obfuscated when ion concentrations are significantly different.

Normalizing the fluxes by the concentrations can sidestep this issue to yield a more representative metric for membrane ion selectivity (the treatment can similarly be applied to transport numbers) (Sata, 2000; Sata et al., 2002; Tanaka, 2015; Luo et al., 2018). When electromigration dominates over diffusion and convection, ion flux of Eq. (3) approximates to $J_i \approx -z_i eu_i^m c_i^m d\phi^m/dx$. Because all ions are driven by the same transmembrane electrostatic potential gradient of $d\phi^m/dx$, the ratio of the concentration-normalized fluxes can be expressed as:

$$S_{ij} \equiv \frac{J_i c_j^s}{J_j c_i^s} \approx \frac{K_i z_i u_i^m}{K_j z_j u_j^m} = \frac{\gamma_i^s \gamma_j^m}{\gamma_j^s \gamma_i^m} \exp \left[-\frac{(z_i - z_j) F}{RT} \Delta \phi_D \right] \frac{z_i u_i^m}{z_j u_j^m}. \quad (4)$$

Substitution of Eq. (1) into Eq. (4) relates the bulk solution concentrations, c^s , to ion concentrations within the IEM, c^m , through sorption coefficients, K .

Further defining sorption selectivity to be the ratio of the sorption coefficients, $K_i/K_j = \gamma_i^s \gamma_j^m (\gamma_j^s \gamma_i^m)^{-1} \exp[-(z_i - z_j) \cdot \Delta \phi_D F / (RT)]$, and migration selectivity to be the ratio of the products of ion valence and absolute mobility, $z_i u_i^m / (z_j u_j^m)$, the concentration-normalized ion transport selectivity of Eq. (4) is, therefore, the products of sorption selectivity and migration selectivity (when electromigration is the dominant transport) and will be termed separation selectivity, S_{ij} . Hence, separation selectivity in IEMs can be achieved through differences in sorption and migration between ions i and j . Specifically, ion valence, z , activity coefficient, γ^m , and absolute mobility, u^m , of the ions in the membrane are the principal factors to affect ion differentiation (γ^s is a solution property). The concepts of sorption and migration selectivities will be the basis of subsequent discussions on the ion-discriminating capabilities of IEMs.

2.3 Permeability-selectivity tradeoffs

In addition to separation selectivity, S_{ij} , permeability of the membrane to the ion of interest is another crucial performance metric for most IEM processes, with the exception of a few applications. Membrane permeance is conventionally defined as the flux per unit driving force (further multiplying permeance by membrane thickness

gives permeability) (Baker, 2012; Geise et al., 2014b). Area-specific resistance or ionic conductivity are often alternatively reported to describe the permeability of IEMs to ion transport (definitions of the terms and their differences from ion permeance are detailed in literature) (Strathmann, 2004; Berezina et al., 2008; Fan and Yip, 2019). Here, ionic conductivity, κ_i , will be taken to be specific to the ion of interest, as denoted by the subscript, instead of being based on the typical net ionic current, which does not distinguish between the contributions from individual charged species. Note that ionic conductivity is not an intrinsic property of the IEM but, rather, is dependent on the operating conditions, including concentrations of the bulk solutions (Długołęcki et al., 2010a; Geise et al., 2014a; Kamcev et al., 2018b; Fan and Yip, 2019).

Higher κ_i signifies faster kinetics, as ion i is transported across the IEM at greater rates for a certain membrane area. Therefore, to achieve a target separation yield, an IEM more conductive to i would require less membrane area, potentially lowering the capital cost (of which membrane stack is a significant contributor) (Strathmann, 2010; Strathmann et al., 2013). Alternatively, the same ion flux can be obtained using smaller driving forces for IEMs with high κ_i , thus lowering energy demand and operating expense of the separation (product of external applied voltage and ionic current yields power consumption). High conductivity of the membrane to target ion i is, thus, universally advantageous.

However, a tradeoff between conductivity and selectivity has been reported in previous IEM studies. Specifically, empirical evidence indicates that an increase in ionic conductivity is accompanied by a concomitant decrease in selectivity for counterions over co-ions (Długołęcki et al., 2008; Geise et al., 2013; Güler et al., 2013; Fan et al., 2020; Russell et al., 2020). The underlying cause was attributed to changes in volume fraction of water in the IEM simultaneously affecting the pathways for ion transport and also altering the density of fixed charges (Geise et al., 2013; Fan and Yip, 2019). Such tradeoff relationships between permeability and selectivity appear to be ubiquitous and have been established for other membrane processes of gas separation, reverse osmosis, and ultrafiltration (Freeman, 1999; Mehta and Zydney, 2005; Robeson, 2008; Kanani et al., 2010; Geise et al., 2011; Siddiqui et al., 2016; Park et al., 2017; Chen et al., 2021). Therefore, it is very plausible that efforts to enhance the selectivity of IEMs may incidentally incur reduced κ_i (Kamcev, 2021).

This putative tradeoff in IEMs can be understood through the governing equations of the sorption-migration transport. Improved flux of ion i and, equivalently, κ_i can be attained by increasing the concentration or absolute mobility of i within the membrane matrix, c_i^m and u_i^m , respectively (Eq. (3)). The sorption of i into the membrane is determined by the activity coefficient,

specifically $c_i^m \propto 1/\gamma_i^m$ (Eq. (1)). Therefore, low γ_i^m and high u_i^m are desired for enhanced κ_i . At the same time, improved selectivity of the membrane for ion i over j can be attained by enhancing the relative sorption, K_i/K_j , which is reciprocally proportional to the activity coefficient ratio, γ_i^m/γ_j^m , or by increasing the absolute mobility ratio, u_i^m/u_j^m (Eq. (4), setting aside the influence of ion valence, z); i.e., low γ_i^m/γ_j^m and high u_i^m/u_j^m are favorable. However, γ and u might not be entirely independent of each other. γ reflects excess partial free energy of the ion in the membrane and comprises enthalpic and entropic contributions (Freger, 2020). Interactions of the ion with solvating molecules, fixed charges, and other mobile ionic species in the membrane relative to the bulk solution change the enthalpy. On the other hand, entropy can be altered when ion translation, rotation, or vibration is sterically hindered in the IEM. Depending on the underlying principles utilized, an approach to alter ion transport may simultaneously affect both sorption and migration of i and j , such that while selectivity, signified by $\gamma_j^m u_i^m / (\gamma_i^m u_j^m)$ in this analysis, is improved, the conductivity of species i , represented by u_i^m/γ_i^m here, is detrimentally lessened. The implications of ion sorption and migration for the conductivity-selectivity tradeoff are further highlighted in the next sections.

A use for IEMs that requires high selectivity but not necessarily high conductivity is application in sensors, e.g., ion-selective electrodes. The primary objective of most IEM applications, e.g., electrodialysis desalination, fuel cells, electrolyzers, and redox flow batteries, is to separate or transport ions from solvent, other ions, and/or other dissolved constituents. Hence, the rate is crucial to overall performance. In contrast, the main aim of sensors is to detect and quantify a specific ion in the solution. Therefore, being able to accurately identify the target ion and characterize the concentration against a sea of background species is more important. By utilizing the open-circuit voltage as the measurement input, sensors can readily operate with minuscule fluxes (De Marco et al., 2007). Aside from sensors, high κ_i is advantageous for almost all other applications of IEMs. Hence, attention should be paid to any accompanying changes in conductivity as selectivity is enhanced.

3 Ion/ion selectivities

This section reviews the ion/ion differentiating capabilities of IEMs, specifically charge selectivity, valence selectivity, and specific ion selectivity. Applications that will benefit from the higher selectivities are highlighted, and the current statuses are discussed. The roles of sorption and migration on the individual selectivities and the tradeoffs with permeability are examined. The technical prospects of approaches to advance the selectivities are then evaluated.

3.1 Charge selectivity

The principal separation capability of IEMs is charge selectivity, i.e., discriminating between positively and negatively charged species. Specifically, cation and anion exchange membranes, CEMs and AEMs, preferentially allow the passage of cations and anions, respectively (Fig. 2(a)). Charge selectivity is the main separation function utilized in the leading IEM applications of the chloralkali process (uses CEMs to allow Na^+ transport from the anolyte to the catholyte while excluding Cl^- and OH^-) and electrodialysis for desalination and ultrapure water production (employs alternative pairs of CEMs and AEMs for the permeation of cations and anions out of a saline feed stream) (Strathmann, 2004; Xu, 2005; Strathmann et al., 2013). Other small-scale and emergent applications include diffusion dialysis acid/base recovery, hydrogen and direct methanol fuel cells, and reverse electrodialysis power generation (Strathmann, 2004; Strathmann et al., 2013; Ran et al., 2017; Jarin et al., 2023).

Charge selectivity is achieved by the characteristic negatively or positively charged fixed functional groups

of CEMs and AEMs, respectively. The selectivity mechanism can be intuitively understood by charge attraction and repulsion. Using CEM to illustrate, the negatively charged moieties attract cationic counterions into the membrane and repel anionic co-ions (Fig. 2(b)). In other words, counterion enrichment and co-ion exclusion are achieved through sorption selectivity, with ion concentrations within the membrane matrix described by a simplification of Eq. (1): $c_i^m \propto c_i^s \exp(-z_i \Delta \phi_D F / RT)$. Because counter- and co-ions are oppositely charged (i.e., z_{ct} and z_{co} have opposite signs) and both experience the same Donnan potential, $\Delta \phi_D$, the exponential terms for c_{ct}^m and c_{co}^m are correspondingly greater and less than 1 ($\Delta \phi_D < 0$ for CEMs and > 0 for AEMs). The mechanism of IEMs to reject co-ions is, hence, termed Donnan or charge exclusion. The sorption selectivity for counterions over co-ions is then $K_{\text{ct}}/K_{\text{co}} \propto \exp[(z_{\text{co}} - z_{\text{ct}}) \Delta \phi_D F / (RT)]$, which reveals the role of ion valence. Specifically, co-ions with higher $|z_{\text{co}}|$ are excluded more from the IEM matrix (counterion sorption is not further enhanced as c_{ct}^m is bound by c_{fix}^m to satisfy electroneutrality, Eq. (2); the role of z_{ct} on valency selectivity is discussed in the next section). Activity coefficient, γ , also affects sorption (Eq.

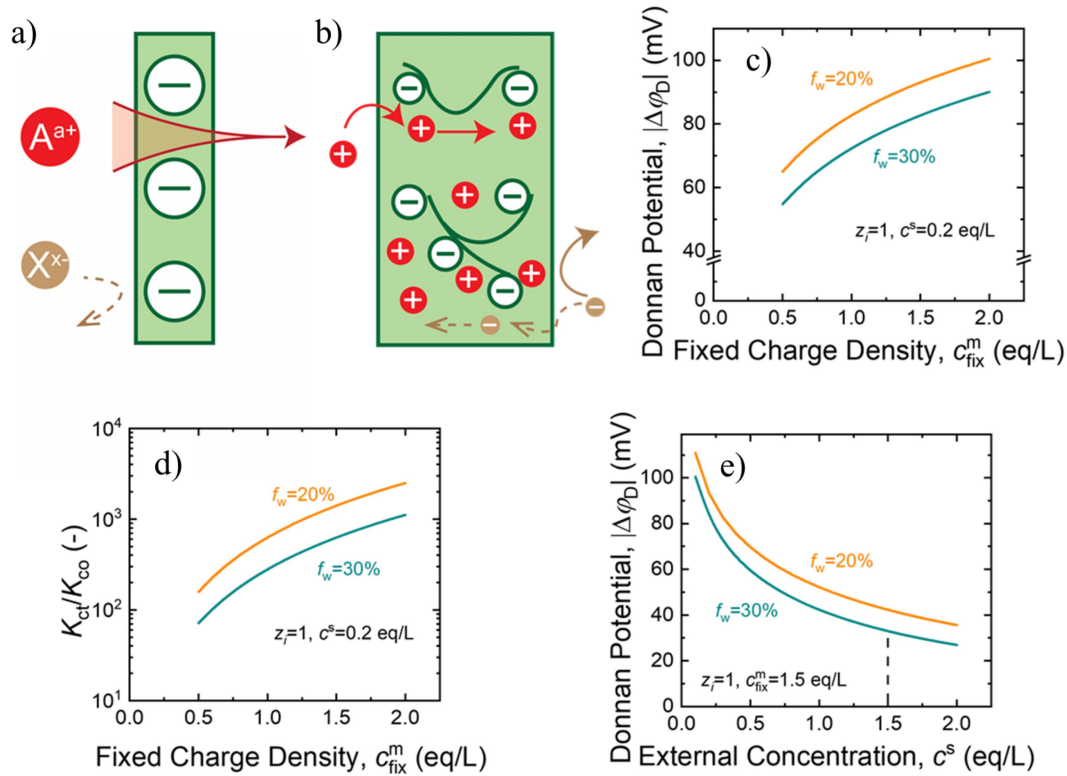


Fig. 2 (a) Schematic illustrating IEM charge selectivity. For a cation exchange membrane, counterion A of valence $a +$ is selectively transported, whereas co-ion X of valence $x -$ is excluded (red and brown circles, respectively). (b) Schematic illustrating the attraction of counterions (cations) and repulsion of co-ions (anions) by the negatively-charged groups of a cation exchange membrane. (c) Representative interfacial Donnan potential, $\Delta \phi_D$, as a function of membrane fixed charge density, c_{fix}^m . (d) Representative sorption selectivity for counterions over co-ions, $K_{\text{ct}}/K_{\text{co}}$, as a function of c_{fix}^m . (e) Representative $\Delta \phi_D$ as function of bulk solution concentration, c^s . Parameters for the analysis are presented in the legends. z_i of counter- and co-ion are $+1$ and -1 , respectively. $\gamma_{\text{ct}}^s \gamma_{\text{co}}^m (\gamma_{\text{co}}^s \gamma_{\text{ct}}^m)^{-1}$ is assumed to be unity.

(1)), but plays a secondary role in charge selectivity (the effect of γ on S_{ij} is further analyzed in a later section). Because u^m of counter- and co-ions with the same valency are typically within a factor of 3, the influence of migration selectivity on separation selectivity is relatively minor compared to sorption selectivity (Kamcev et al., 2018a). Overall, the selective transport of counterions over co-ions in IEMs is governed by charge through sorption of the ions to sorb into the membrane matrix under a Donnan potential.

IEM selectivity for counterion transport is frequently quantified by the metric of permselectivity, commonly defined based on transport numbers: $(t_{ct}^m - t_{ct}^s)/(1 - t_{ct}^s)$ (Luo et al., 2018), with values of unity and zero signifying perfect exclusion of co-ions and complete absence of charge selectivity, respectively. Because co-ions are typically highly excluded from the IEM, c_{co}^m is usually smaller than c_{ct}^m by several orders of magnitude. Additionally, permselectivity is almost always characterized using 1:1 electrolytes such as NaCl and, therefore, c_{ct}^s and c_{co}^s are equal. These two characteristics, hence, mitigate the relative prevalence issue of different ions raised earlier in the Ion Selectivity section. Description of methods to characterize permselectivity can be found in literature (Strathmann, 2004; Luo et al., 2018; Geise, 2020). Reported permselectivities for high-performing commercial IEMs range between 0.82 and 0.99 for CEMs and 0.86–0.93 for AEMs (characterized using 0.1 and 0.5 mol/L NaCl electrolytes) (Długołęcki et al., 2008; Długołęcki et al., 2010b; Vermaas et al., 2011; Güler et al., 2012; Güler et al., 2013; Tong et al., 2016).

Enhanced charge selectivity is primarily obtained through having high densities of membrane fixed charges, c_{fix}^m , which raises $|\Delta\phi_D|$ to exclude more co-ions, as depicted in Figs. 2(c) and 2(d) (Eqs. (1) and (2)). The ratio of co-ions to counterions within the IEM, c_{co}^m/c_{ct}^m , approximately scales with $(c_{fix}^m)^{-2}$ (Fan and Yip, 2019). Additionally, ionic conductivity of the IEM is also beneficially improved, as greater c_{fix}^m yields more charged species within the membrane matrix to carry the ionic current (Geise et al., 2013; Fan and Yip, 2019). In practice, however, efforts to improve permselectivities (and ionic conductivities) by increasing membrane fixed charge density are chemically and physically constrained. Intensifying the density of fixed charges increases hydrophilicity of the polymer matrix and consequently increases the membrane swelling (Heintz et al., 1997; Wiedemann et al., 1998). Swelling of the IEM volume dilutes c_{fix}^m and thus has a self-limiting effect on charge selectivity (Fan and Yip, 2019).

Permselectivities of commercially available IEMs are adequate for the range of bulk solution concentrations employed in the current applications. However, co-ion exclusion is inversely related to the bulk-phase electrolyte concentration: higher c^s reduces $|\Delta\phi_D|$ (Fig. 2(e)), which diminishes Donnan exclusion and consequently lowers

permselectivity (Eqs. (1) and (2)). When c^s approaches c_{fix}^m , ability of the IEM to differentiate between counter- and co-ions is severely diminished, and permselectivity drops drastically (vertical dashed line of Fig. 2(e)) (Fan and Yip, 2019). Extending the electrolyte concentration range in which IEMs still operate with high permselectivities can tip the energy-efficiency and cost-effectiveness scales and enable IEMs to access new applications, such as electrodialysis of high-salinity brines, bipolar membranes for hypersaline water dissociation, redox flow batteries with concentrated anolytes and catholytes (suppressing reactant crossover), and electrodialysis metathesis for chemical synthesis (Tongwen, 2002; Jaroszek and Dydo, 2016; Ran et al., 2017; Parnamae et al., 2021). Strategies to improve permselectivity by increasing c_{fix}^m will need to work within the constraint of membrane swelling described above. Simultaneously crosslinking the polymer matrix while increasing the fixed charge density can restrain membrane swelling (Zhou et al., 2017a; Zhu et al., 2019). Incorporating more charged moieties will raise the membrane hydrophilicity and exert mounting osmotic swelling pressure on the polymer network. Beyond a certain point, the expansion stress can exceed the mechanical stability of the crosslinking, and the polymer matrix ceases to form the required thin film (Lakshminarayanaiah, 1965; Meares, 1986). Additionally, the functionalization chemistry will also ultimately impose an upper limit on the achievable concentration of charged moieties (Takamuku et al., 2015).

3.2 Valence selectivity

Beyond charge-based selectivity, i.e., between cations and anions, IEMs can be employed to separate like-charged ions with different valences (Fig. 3(a)). Applications include: production of table salt (NaCl) from seawater, segregation between Li^+ and Mg^{2+} in lithium-rich brines, removal of Ca^{2+} , Mg^{2+} , and other polyvalent cations from Na^+ and K^+ for water softening and scale control, isolation of Na^+ from divalent cations in irrigation water treatment, removal of hazardous polyvalent oxyanions such as arsenate and selenate from other monovalent anions for water purification, segregation of H^+ from heavy metal ions for acid recovery from industrial waste streams, orthophosphate recycling from wastewaters, redox flow batteries, and general fractionation of ions based on valence (Sata, 2004; Strathmann, 2004; Van der Bruggen et al., 2004; Strathmann et al., 2013; Tran et al., 2014; Chen et al., 2015; Nie et al., 2017b; Ahdab et al., 2021; Amiri et al., 2021; Yan et al., 2022), although presently few are widely adopted mainstream processes (table salt production in Japan is an exception). As evident from Eqs. (1), (3), and (4), ion valence influences both sorption and migration selectivities. In other words, the valency

affords opportunities through both mechanisms of sorption and migration to affect relative transport between different counterions.

Inspection of the sorption selectivity, $K_i/K_j \propto \exp[-(z_i - z_j)\Delta\phi_D F/(RT)]$, reveals that counterions of higher valence, z , are more enriched in the membrane matrix for mixed electrolyte bulk solutions (Fig. 3(b)). The phenomenon can be intuitively understood by the stronger coulombic attraction of species with larger $|z|$ to the opposite polarity fixed functional groups of the IEM. However, the effect is diminished with increasing concentrations of the external electrolytes. As discussed previously, $|\Delta\phi_D|$ is depressed at elevated c^s (Fig. 2(e)). The lowered magnitude of $\Delta\phi_D$ reduces the ability of the IEMs to preferentially sorb higher valence counterions (Fig. 3(c)).

Ion valence also impacts migration selectivity, $z_i u_i^m / (z_j u_j^m)$. Under the same transmembrane electrostatic

gradient, $d\phi^m/dx$, counterions experience driving forces for electromigration that is proportional to z (Eq. (3)), as described by the classic Coulomb law. However, absolute ion mobility, u^m , is a more dominant factor in electromigration. The fixed charge groups anchored to the polymer backbone and mobile counter- and co-ions in the membrane matrix are essentially point charges that each exerts an electric field. These electrostatic interactions impose friction-like losses on permeating ionic species, retarding their movement across the IEM and resulting in reduction of the effective mobilities. Our previous work showed that u^m is related to $u^s \exp(-Az^2)$, where A is an aggregated parameter of c_{fix}^m , permittivity, temperature, universal constants, and a conversion coefficient (Fan et al., 2022). Critically, u^m decays exponentially with z^2 . The mobility impediment due to the electrostatic interactions experienced by higher valence ions are, therefore, much more severe and quickly overwhelms

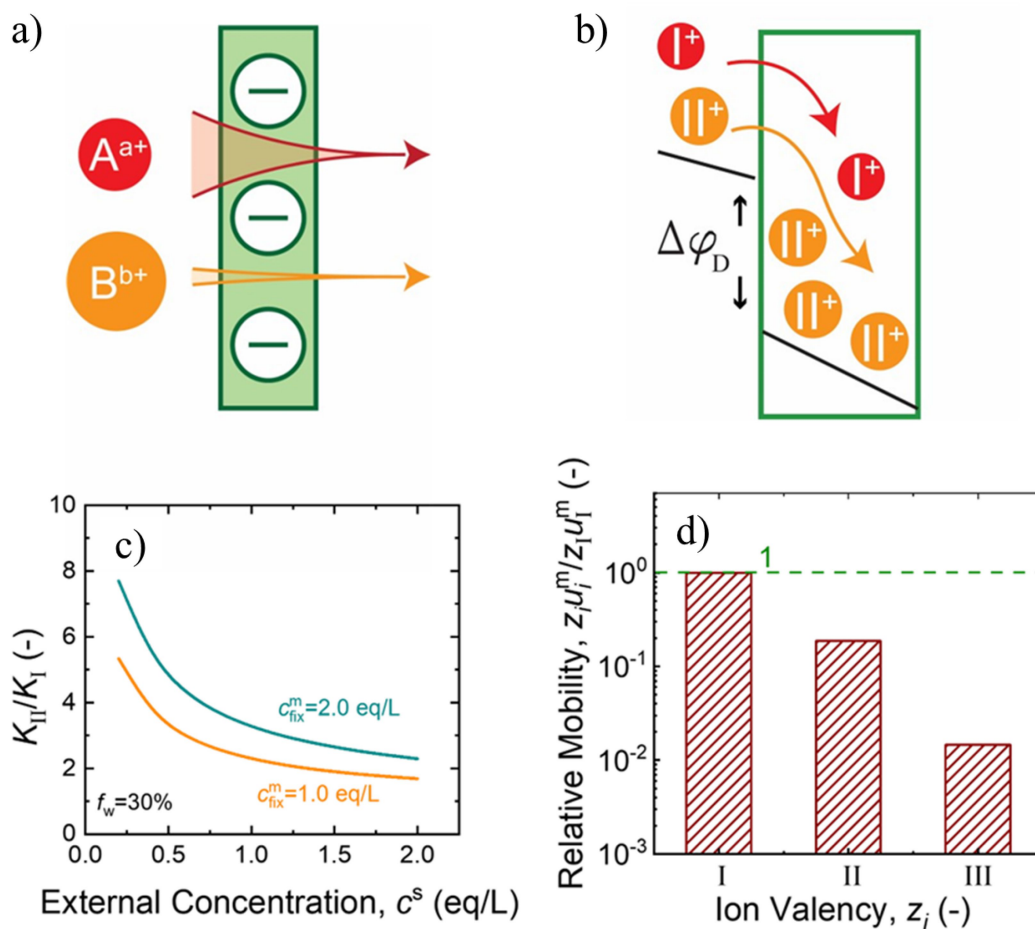


Fig. 3 (a) Schematic illustrating valence selectivity between counterion A and B with like (positive) charge but different valences of a and b (i.e., $a \neq b$), respectively (red and yellow circles). (b) Schematic depicting sorption selectivity of a highly charged cation exchange membrane toward high-valence counterions at interfacial Donnan potential $\Delta\phi_D$. (c) Representative sorption selectivity for divalent counterions over monovalent counterions, K_{II}/K_I , as a function of external bulk concentration, c^s , with mono- and divalent ions at the same equivalent concentrations. (d) Representative migration selectivities of mono-, di- and trivalent counterions relative to the monovalent counterion, $z_i u_i^m / (z_1 u_1^m)$.

mobility increases from the linear Coulombic relation (Fig. 3(d)). Overall, migration selectivity favors lower valency counterions in electromigration-dominated transport.

The effects of z on sorption and migration selectivities are, hence, opposing: counterions with higher $|z|$ are preferentially sorbed into the IEM but are more impeded by the electrostatic interactions. Generally, the effect of sorption selectivity is stronger than migration selectivity at lower external solution concentrations and the membrane is more selective for higher $|z|$ counterions. But preferential transport of higher valence ions is weakened at higher c^s as sorption selectivity is diminished. As an illustration, S_{ij} for divalent Ca^{2+} over monovalent Na^+ is ≈ 3.5 at $c^s \approx 0.05$ eq/L but is drastically lowered to ≈ 0.4 at $c^s \approx 4$ eq/L (for commercial CEMs) (Sata et al., 2002).

IEMs that are more selective for monovalent counterion transport are available on the market, with S_{ij} for monovalent Na^+ over divalent Ca^{2+} ranging from ≈ 3 –15 (at $c^s \approx 0.05$ –0.5 eq/L) (Saracco, 1997; Ahdab et al., 2020; Ahdab et al., 2021). Two main approaches are typically employed to achieve the selective transport of monovalent counterions over polyvalent species. The first approach utilizes the greater exclusion of higher valency co-ions (discussed in the previous section). Readers are directed to literature for more detailed discussions of the mechanism (Sata et al., 2002; Luo et al., 2018; Tang and Bruening, 2020; Wang et al., 2022a; Wang et al., 2022c). Briefly, IEMs are coated with a surface layer with oppositely charged functional groups or layer-by-layer assembly of alternately charged polyelectrolytes. The working principles can be understood by considering the example of negatively charged CEM modified with a positively charged surface film. Co-ions of the oppositely charged layer, i.e., cations in the illustrative example, are counterions of the main IEM. Thus, in the coating layer, concentrations of higher $|z|$ cations are disproportionally reduced because of the greater charge exclusion of co-ions ($c_{\text{co}}^m \propto c_{\text{co}}^s \exp(-z_{\text{co}} \Delta \phi_D F / (RT))$). That is, the coating layers possess sorption selectivity for lower valency cations, resulting in disproportionally greater reductions in net ionic conductivities for higher $|z|$ cations across the coated membrane. Hence, the modified membranes are overall more selective for monovalent than polyvalent ions.

The second approach utilizes dense coating layers to increase the steric hindrance of polyvalent counterions (Luo et al., 2018). Because of the higher charge density, di- and trivalent ions have larger hydrated ion sizes (and greater hydration free energies, ΔG_{hyd}) than monovalent ions. Therefore, polyvalent ions experience relatively higher steric hindrance during transport across the dense modification films (Sata, 2000; Sata et al., 2002; Luo et al., 2018). The reduced mobility can be explained using the free volume theory commonly used in IEM studies,

which states that u^m scales reciprocally with the exponential of the ratio between the minimum free volume occupied by the permeant and the total membrane free volume (Yasuda et al., 1968; Yasuda et al., 1971; Luo et al., 2020). Other membrane transport theories, such as the hindered transport model of nanofiltration, similarly predict the same influences on species of different sizes (Wang et al., 2014b; Wang and Lin, 2021). Constricting the membrane free volume, therefore, hampers ion permeation, i.e., reduces u^m , with larger hydrated ions more severely impacted. But transport of monovalent ions is also hindered, albeit to a lesser extent.

In the first approach, κ_i of monovalent counterions across the overall membranes are also detrimentally reduced because their very low concentrations as co-ions in the oppositely charged modification layers. Therefore, in both the oppositely charged and dense surface layers approaches, the ionic conductivities of monovalent counterions are depressed. In other words, the improved selectivity for monovalent over polyvalent ions is achieved at the expense of lower ionic conductivity, i.e., permeability-selectivity tradeoff.

Enhancing the valence selectivity of IEMs can broaden implementation of the applications mentioned earlier. Membrane differentiation between counterions with different valences can be tuned through the migration selectivity (Eq. (4)). Our previous work indicated that absolute ion mobilities are affected by electrostatic interactions, with u^m being reciprocally dependent on the exponential of $(c_{\text{fix}}^m)^{2/3}$ and ε^{-2} , where ε is permittivity experienced by the permeating ions within the IEM matrix (Fan et al., 2022). Therefore, increasing the membrane fixed charge densities and reducing the dielectric of the local environment in the hydrated nanoscale channels can, in principle, exaggerate the retardation of species with higher $|z|$, with lower valency counterions impeded to smaller extents. As mentioned earlier, raising c_{fix}^m intensifies the Donnan exclusion effect (larger $|\Delta \phi_D|$) and hence raises IEM affinity for higher $|z|$ counterions (Eq. (1)), i.e., opposite effect to migration selectivity. By thoughtful control of membrane properties c_{fix}^m and ε , selectivity for lower $|z|$ ions can potentially be increased, with some sacrifice in κ_i .

Alternatively, ion valence discrimination can be altered through sorption selectivity by modifying the ion activity coefficient within the IEM, γ^m (Eq. (4)). Compared to monovalent ions, polyvalent ions generally exhibit stronger coordination with ligands. The incorporation of ligating functional groups that preferentially interact with target polyvalent ions, e.g., Cu^{2+} , can increase the sorption selectivity by lowering γ^m of the favored species (i.e., the mechanism is not directly due to the electrostatic effects of z) (Sata et al., 2002). However, as the mobility of more strongly associated species is also retarded, the improved S_{ij} is, again, obtained at the cost of diminished κ_i for the preferentially complexed counterion. The

nuanced factors of utilizing coordination chemistry to enhance selectivity are further discussed in the next section.

3.3 Specific ion selectivity

The development of IEMs capable of distinguishing between counterions with the same valence will enable specific ion selectivity (Fig. 4(a)). However, as the sign and integer of the valence are identical for the species to be separated, ion charge cannot be the primary differentiating feature for separation, unlike the preceding charge and valence selectivities, and S_{ij} of Eq. (4) reduces to $\gamma_i^s \gamma_j^m u_i^m / (\gamma_j^s \gamma_i^m u_j^m)$. Therefore, specific ion selectivity is the most technically difficult to achieve, and there are no such membranes available in the market at present. The poor discrimination of conventional commercial IEMs is reflected in the low S_{ij} s. For example, S_{ij} ranges ≈ 0.4 – 1.2 for the separations of Li^+/K^+ , $\text{Cu}^{2+}/\text{Zn}^{2+}$, and $\text{NO}_3^-/\text{Cl}^-$ (Ersöz, 1995; Cruz et al., 2000; Deng et al., 2014; Nie et al., 2017a; Mubita et al., 2020; Sharma et al., 2020; Kong et al., 2022). H^+ and OH^- ions are exceptions. Because of the Grotthuss mechanism and local recombination of the hydrogen bond network (Luo et al., 2018), respectively, H^+ and OH^- ions are significantly more mobile in water, with bulk-phase diffusivities $\approx 5\times$ and $\approx 2.5\times$ greater than other monovalent species (Strathmann, 2004; Luo et al., 2018). As such, higher selectivities are achievable by conventional IEMs for H^+ and OH^- over other monovalent cations and anions, respectively (for example, Nafion has demonstrated selectivity of 4–6 for H^+/Na^+ and H^+/K^+) (Miyoshi, 1997). As such, H^+/M^+ and OH^-/X^- selectivities will not be priorities for this review of specific ion selectivity.

Potential applications that can benefit from enhanced selectivities between ions of the same valence include: isolation of Li^+ from Na^+ and K^+ (The White House, 2018; Warren, 2021), recovery of nutrients NO_3^- , NH_4^+ , and $\text{H}_2\text{PO}_4^{x-3}$ from wastewaters containing other ions of the same valences (Li et al., 2015; Xu et al., 2018; McCartney et al., 2021), removals of trace contaminants from drinking water, e.g., arsenic as dihydrogen arsenate, H_2AsO_4^- , and lead, Pb^{2+} , from monovalent anions and divalent cations, respectively (Clark et al., 2016; Tirrell et al., 2017), separation between Co^{2+} and Ni^{2+} for battery recycling (Huang et al., 2019; Alvial-Hein et al., 2021), recovery of specific transition metals from other divalent cations in industrial waste streams (such as coal ash) (The White House, 2022), segregation of lanthanide ions (Tang and Bruening, 2020), and harvesting of uranyl ions, UO_2^{2+} , from Ca^{2+} and Mg^{2+} in seawater (Kim et al., 2013; Wang et al., 2020).

Coordination chemistry has been investigated to enhance relative transport of the target species. Ligands

with preference to reversibly complex with an ion can act as ionophores (Greek for ion carriers), enabling the ion to “hop” from site to site (Fig. 4(b)) (Cussler et al., 1989). As such, specific coordination chemistry can be utilized to differentiate between counterions with the same valence and selectively transport a certain ionic species over others. Ligating functional groups that have been studied include iminodiacetate for selective Cu^{2+} transport over divalent cations (Mg^{2+} , Ca^{2+} , Co^{2+} , Ni^{2+} , and Zn^{2+}) and crown ethers for K^+/Li^+ and Cs^+/Na^+ separations (the chemistries were also investigated for selective salt transport in uncharged membranes) (Chaudhury et al., 2014; Sheng et al., 2014; Tas et al., 2016; Warnock et al., 2021; DuChanois et al., 2022). With incorporation of the ligating function groups, sorption selectivity for the specific ion is enhanced, i.e., γ_i^m is advantageously lowered, and the membrane matrix is enriched with the target species. However, because of the strong complexation interactions with the ligating group, mobility of the specific ion is deleteriously reduced, i.e., u_i^m is lowered. Thus, ligand-ion interaction free energy is a key factor governing γ^m and u^m of the target ion and also of other charged mobile species (Zofchak et al., 2022). The net effect on S_{ij} , hence, depends on the modifications to γ_i^m , γ_j^m , u_i^m , and u_j^m , and the eventual outcome on separation selectivity can swing either way. While the previous studies reported selective transport of the complexed ion (Chaudhury et al., 2014; Sheng et al., 2014; Tas et al., 2016; DuChanois et al., 2022; Sachar et al., 2022), a recent atomistic molecular dynamics simulation found that coordination chemistry will actually favor the transport of noncomplexing species (Zofchak et al., 2022). The reversal in trend is caused by exceedingly strong ligand-ion interactions drastically retarding mobility of the coordinated ion, overwhelming the benefits of higher partitioning. This observation suggests that net ionic conductivity, which is the combination of sorption and migration, is maximized at a certain ligand-ion interaction free energy (Fig. 4(c)), analogous to the Sabatier principle of heterogeneous catalysis (Medford et al., 2015). Similarly, the separation selectivity between species i and j should also be optimized with respect to the interaction free energies between the ligand and the two ions. S_{ij} as high as ≈ 52 for $\text{Cu}^{2+}/\text{Mg}^{2+}$ and ≈ 14 for K^+/Li^+ were reported in the studies (determined using diffusion dialysis, Donnan dialysis, or electrodialysis), considerably better than conventional IEMs (Chaudhury et al., 2014; Sheng et al., 2014; Tas et al., 2016; DuChanois et al., 2022). However, κ_i of the preferentially transported counterions were not reported, and it remains to be seen if the improved selectivity was achieved at the expense of permeability.

Instead of being immobilized on the polymer backbone, ligands can be dispersed in organic solvents impregnating porous substrates to form supported liquid membranes (Fig. 4(d)) (Kocherginsky et al., 2007; San Román et al.,

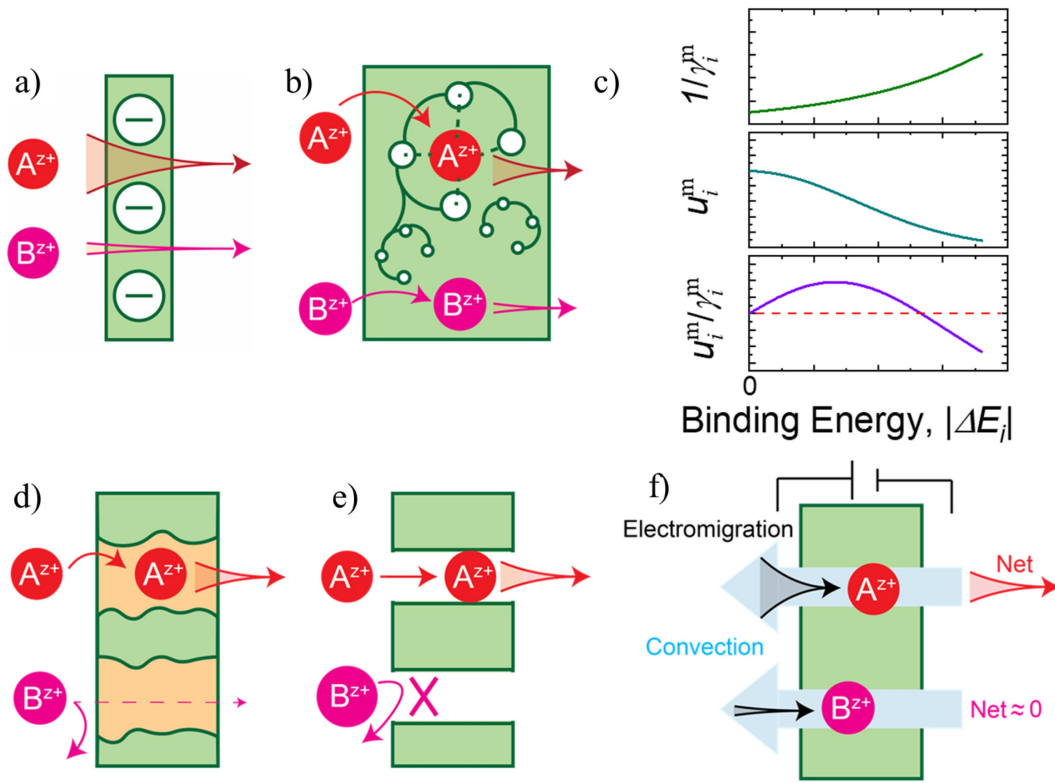


Fig. 4 (a) Schematic illustrating specific ion selectivity, in which the cation exchange membrane differentiates between counterions A and B of the same valence $+z$ (red and magenta circles). (b) Schematic illustrating coordination chemistry for specific ion selectivity. (c) Representative plots showing the influence of ligand-ion interaction energy on sorption, migration, and net separation selectivity: inverse of membrane activity coefficient, $1/\gamma_i^m$, membrane mobility, u_i^m , and their product, u_i^m/γ_i^m , as functions of ligand-ion binding free energy, $|\Delta E_i|$. (d) Schematic illustrating ion-selective transport in supported liquid membranes, with orange shaded regions denoting impregnating solvent in the porous membrane. (e) Schematic illustrating size sieving between same-valency counterions with slightly different dimensions. (f) Schematic depicting the tuning of electromigration and convection (black and blue arrows, respectively) for ion-specific separation. The opposing electrically-driven and advective fluxes yield a nonzero net flux for A and a near-zero net flux for B, resulting in overall transport selectivity for A over B.

2010; Parhi, 2013). This approach takes advantage of the sorption selectivity while sidestepping some of the reductions in mobility as the ligand-ion complexes are now mobile (i.e., mobility of the complexes in the organic solvent influences overall transport). Supported liquid membranes with weakly coordinating anions as the facilitated cation carriers showed S_{ij} of 1–10 and 700–800 for the preferential transport of K^+ over Na^+ and Li^+ , respectively, in electrodialysis (Qian et al., 2020; Qian et al., 2022). The studies suggested that partial dehydration of the ions also plays a role in influencing selectivity, with ions that hold on to their shell of hydrating water more weakly (i.e., lower $|\Delta G_{hyd}|$) being favored. However, even with the mobile ligands, conductivities of the supported liquid membranes are $6\text{--}200 \times$ lower than the commercial IEMs.

Ions with identical z tend to have similar hydrated ion sizes, even across mono- and polyatomic species, thus frustrating steric approaches to improve discrimination. For example, the hydrated ion radii of Li^+ and Cs^+ (2nd and 7th periods of alkaline metals) are 3.82 and 3.29 Å,

respectively, a difference of only 16%, with hydrated polyatomic NH_4^+ being 3.31 Å (Nightingale, 1959). The same trend is observed for polyvalent species and anions. Therefore, the general steric exclusion of hydrated ions governed by the free volume theory discussed earlier is unlikely to be sufficient for adequate separation of the species. Materials with more precise subnanometer pores can sidestep the above limitation and utilize size sieving to boost selectivity by drastically increasing γ^m of the larger species (Fig. 4(e)). Because selectivity is achieved by exclusion of the undesired ion (i.e., entropic portion of γ^m) rather than inclusion of the target species through increased specific interactions (which are enthalpic contributions to the activity coefficient), u^m of the target counterion can potentially be uncompromised (Zhang et al., 2018). The introduction of porous metal-organic frameworks into charged polymer matrix showed remarkable specificity for Li^+ over Na^+ and K^+ (selectivity was not explicitly defined in the paper, thus preventing efforts to benchmark the reported values of 35 and 67, respectively) (Guo et al., 2016). However,

effective ionic conductivities of the composite membrane are still drastically lower than conventional IEMs by around three orders of magnitude. Interestingly, the order of preferential transport trended oppositely with hydrated ion size (hydrated Li^+ is the largest but was most selectively transported). The observation was attributed to stronger interactions of the ions with charged functional groups of sulfonated polystyrene causing Na^+ and K^+ to associate less reversibly with the fixed sulfonate moieties, thereby slowing their transport relative to Li^+ . Contradictorily, such pronounced differentiations were not seen in conventional sulfonated polystyrene IEMs. Ion dehydration and framework chemistry are additional factors influencing ion transport, as pointed out by other membrane studies on porous metal-organic frameworks (but not in charged polymers) (Zhang et al., 2018), and may have contributed to the atypical behavior.

Inorganic materials have been investigated for ion selectivity driven by electrostatic potentials. Ceramic membranes based on metal alkoxide and composite membranes with inorganic metal oxide nanoparticle fillers (magnesium doped lithium manganese oxide) in a charged polymer matrix utilize the specificity of ion intercalation/insertion to attain Li^+ selectivity over Na^+ and K^+ (Ohya et al., 1998; Sharma et al., 2020). Membranes fabricated using NASICON (acronym for Na super ionic conductor, with chemical formula $\text{Na}_{1-x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$) showed selectivity between Li^+ , Na^+ , K^+ , and Cs^+ (Cretin and Fabry, 1997; Mauvy et al., 1999; Fountain et al., 2008). But, again, selectivity metrics different from S_{ij} were reported in these studies, thwarting comparisons with reference membranes. The membranes generally have considerably lower κ_i than conventional IEMs. NASICON membranes, for instance, were primarily investigated for sensor applications, although a recent study demonstrated membrane conductivity within an order of magnitude of commercial CEMs (and very high selectivity for Na^+ over divalent Ca^{2+} and Mg^{2+}) (Kim et al., 2022b).

Biological ion channels can achieve very high specific ion selectivities with simultaneously fast kinetics of ion transport, i.e., in defiance of the conductivity-selectivity tradeoff constraining synthetic IEMs (Gouaux and MacKinnon, 2005; Zhou et al., 2012; Acar et al., 2019; Epsztein et al., 2020; DuChanois et al., 2022). For instance, natural potassium ion channel KcsA has S_{ij} as high as 10^4 for K^+ over Na^+ (Noskov et al., 2004). Biomimetic and bioinspired channels for selective ion transport have been actively researched (Barboiu et al., 2014; Gilles and Barboiu, 2016; Ren et al., 2017; Barboiu, 2018; Acar et al., 2019; Liu et al., 2021). A recent study incorporated biomimetic channels of crystalline porous organosulfonate-amidinium salts into polyimide membranes and demonstrated impressive separation selectivities of 360, 32, 110, and 1300 for K^+ over Li^+ , Na^+ , Rb^+ , and Cs^+ , respectively (Xin et al.,

2022). The preference for K^+ transport was attributed to ion-channel effects of cation- π and electrostatic interactions raising the energy barrier for Li^+ and Na^+ (elements above potassium in the periodic table) and the larger ion radius of the first hydration shell of Rb^+ and Cs^+ (elements below K in the periodic table). But because κ_i was not reported, it is unclear if the permeabilities of the biomimetic membranes can actually compete with conventional IEMs. Other recent studies fabricated bilayer metal-organic frameworks to mimic the Å-scale asymmetrical cavity structures of biological ion channels (Abdollahzadeh et al., 2022; Xiao et al., 2022). Ion current ratios as high as 84 and 80 for K^+/Li^+ and Na^+/Li^+ were reported. However, the selectivity characterizations employed single electrolytes; other membranes utilizing the same mechanism but based on graphene oxide reported selectivity of 3.7 for K^+/Li^+ when mixed salt solutions were used (Ahmadi et al., 2022). Again, ionic conductivity was not explicitly stated; based on the reported characterizations of the metal-organic framework membranes (measured conductance and membrane thickness and area), κ_i appears to be ≈ 3 –4 orders of magnitude lower than conventional IEMs. Compared to what has been attained in nature, specific ion separations with synthetic membranes, biomimetic/bioinspired or otherwise, may be considered in the nascent stages of development.

Notably, most of the strategies explored for specific ion separations were also examined for valence selectivity, usually achieving better performances (An et al., 2019; Shehzad et al., 2019; Li et al., 2020; Kim et al., 2022b; Qian et al., 2022). This is because the ion properties used to discriminate between species are generally more dissimilar between ions with different valences (e.g., higher $|z|$ ions have markedly larger hydrated size, greater $|\Delta G_{\text{hyd}}|$, and stronger interactions with ligands). Overall, broader research on ion sieving materials, such as graphene oxide laminates and nanotubes with subnanometer pores (Abraham et al., 2017; Razmjou et al., 2019; Li et al., 2021), and biomimetic and bioinspired ion transporters (Shen et al., 2014; Epsztein et al., 2020; Tu et al., 2021; DuChanois et al., 2022) can deepen understanding of the mechanisms and inform on the design principles for specific ion and valence selectivity.

Besides membrane development, innovations to the IEM processes can improve specific ion selectivity. Recent studies inventively utilized convective ion flux driven by water permeation, i.e., third term of Eq. (3), to affect net ion transport (Fig. 4(f)) (Tang et al., 2020; Tang et al., 2021). Because counterions of the same valence have small but not insignificant differences in absolute ion mobility (which scales reciprocally with hydrated size), the electromigration terms of the ion fluxes (second term of Eq. (3)) are slightly different (even when concentrations are similar). By setting up electromigration and convection in opposing directions and carefully

controlling the relative magnitudes, the net transport of one ion can be suppressed by having the two terms exactly cancel each other out, while another ion maintains a reduced but nonzero flux, i.e., $J_j \approx 0$ and $J_i \neq 0$, respectively. Because the denominator of S_{ij} approaches zero, separation selectivity between ions i and j can, in principle, be infinitely high (neglecting ion depletion at the solution-membrane interface due to concentration polarization) (Dresner, 1972,1974; Yaroshchuk and Vovkogon, 1994a; Yaroshchuk and Vovkogon, 1994b; Yaroshchuk, 2000a,b; Yaroshchuk, 2008). S_{ij} of 100 and 30 for Li^+ transport over K^+ and Na^+ , respectively, were demonstrated using polycarbonate track-etched membranes with negatively charged pores (Tang et al., 2021) (note that the approximation of S_{ij} in Eq. (4) to the sorption and migration terms is not appropriate here as the assumption that transport is dominated by electromigration is no longer valid). However, as the working principles of the process result in depressed J_i and track-etched membranes have low porosities (typically < 0.1), κ_i of the permeating species is also unavoidably low. That is, the process is still affected by a conductivity-selectivity tradeoff, albeit in a fundamentally different way.

4 Ion/molecule selectivities

Moving on from the ion discriminating capabilities, this section assesses the crossover of uncharged molecules in IEMs, specifically solvents and neutral solutes. The scope and organization of the review are similar to the preceding section, i.e., summary of applications, review of current status, examination of roles of sorption and migration, implications for permeability-selectivity tradeoffs, and appraisal of technical approaches to suppress crossover.

4.1 Ion/solvent selectivity

The principal function of IEMs concerns the transport of ions. However, the transport of solvent is also critical for several applications, but is often overlooked. Solvent transport can occur by osmosis and electro-osmosis across the swollen membranes (Figs. 5(a) and 5(b), respectively). The solvent is primarily water, but can be nonaqueous in some applications. In electrodialysis desalination, diluate stream exiting the stack is the desalinated product water. Therefore, water permeation from the diluate stream, across the membrane, to the concentrate stream represents a direct loss in water recovery performance. This problem is particularly acute for high recovery yield operations and treatment of hypersaline brines, where product water volume can be reduced by as much as half (Rottiers et al., 2014; Yan et al., 2019). In fuel cells, solvent crossover from the

anolyte into the catholyte contributes to flooding of the cathode chamber and can drastically degrade performance (Vielstich et al., 2003; Li et al., 2008). In direct methanol fuel cells, transport of water from the anolyte to the catholyte constrains the amount of methanol in water to very dilute concentrations < 3 mol/L, thus drastically capping the energy densities achievable (Ren and Gottesfeld, 2001; Liu et al., 2006). Additionally, methanol that leaks from the anolyte is lost fuel (cathode performance is also deleteriously impacted when methanol is oxidized by oxygen) (Heinzel and Barragan, 1999; Ahmed and Dincer, 2011). Solvent crossover in aqueous and nonaqueous redox flow batteries causes undesirable imbalances in concentrations and volumes of the anolytes and catholytes, and is the main cause of capacity decay in long-term cycles (Zhou et al., 2017b; Oh et al., 2019). In the above-mentioned applications and others, excessive solvent transport can render the overall process unviable.

Solvent flux can be driven by transmembrane osmotic and hydrostatic pressure differences, $\Delta\pi$ and ΔP , respectively. As practically all applications operate with a solute concentration gradient and, hence, an osmotic pressure difference, IEM processes unavoidably experience an osmotic driving force for solvent flux. On the other hand, most processes are not pressurized (hydraulic pressure differences across the membrane from fluid circulation, if present, are small compared to osmotic pressure differences), with the notable exceptions of water electrolyzers and fuel cells. For simplicity of analysis, ΔP is considered to be negligible and osmotic solvent flux can be described by $J_{w,os} = A_{w,os} \Delta\pi / \Delta l$ (although the solvents can sometimes be nonaqueous, water is still most frequently employed; thus, the notation here will be represented by subscript w, for simplicity in presentation; subscript os denotes osmosis; Δl is membrane thickness). Osmotic water permeability coefficient, $A_{w,os}$, encompasses both sorption and migration (analogous to permeability of the classic solution-diffusion framework being the product of solution and diffusion) (Baker, 2012; Geise et al., 2014b), and for conventional IEMs, $A_{w,os}$ ranges between 0.05–10 $\text{L} \cdot \mu\text{m} / (\text{m}^2 \cdot \text{h} \cdot \text{bar})$ (Xie et al., 2011; Kamcev, 2016; Kingsbury and Coronell, 2021).

Because the driving force for solvent osmosis is different from ion electromigration (osmotic pressure and electrostatic potential gradients, respectively), taking the ratio of ion flux to osmotic flux, or concentration-normalized fluxes, does not cancel out the driving force. Hence, examining S_{ij} is of limited utility and discussions on improving ion/solvent selectivity will, instead, be centered on suppressing solvent transport. Uncharged solvent molecules are not affected by the Donnan potential. The sorption coefficient for water (solvent), $K_w \equiv c_w^m / c_w^s$ (c_w^m is with respect to the entire hydrated membrane volume), is approximately equal to the water

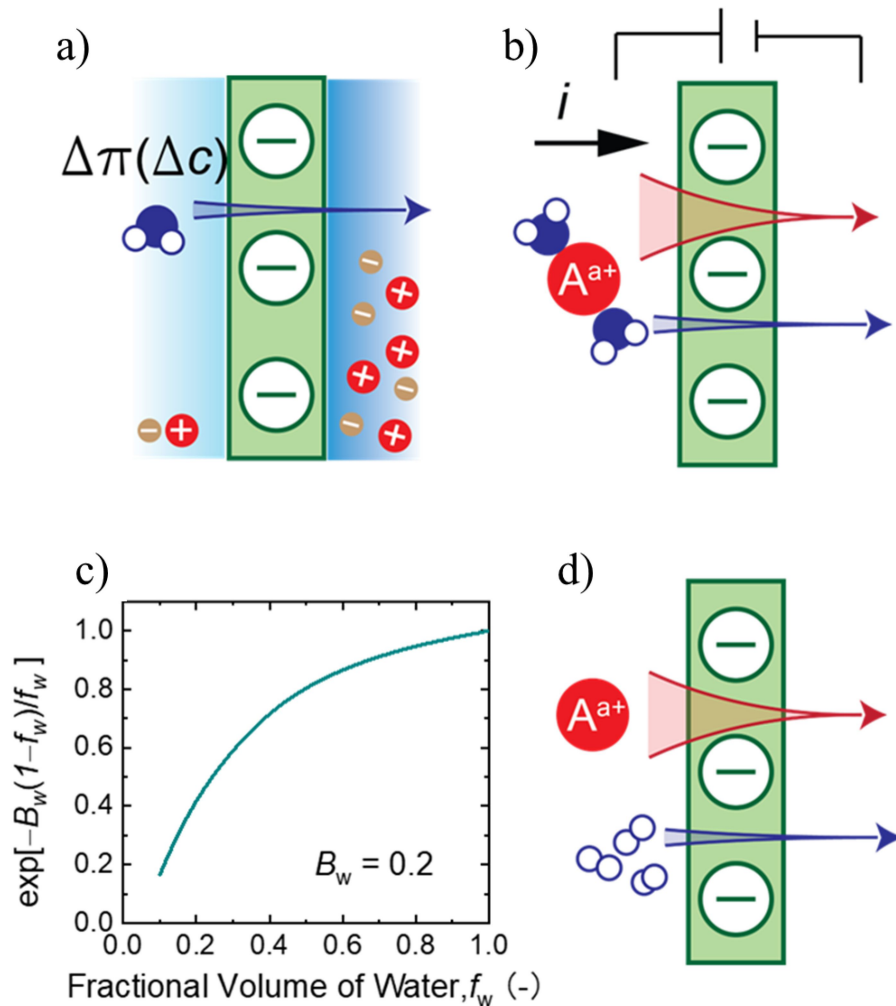


Fig. 5 (a) Schematic illustrating water osmosis driven by the osmotic pressure difference across the membrane, $\Delta\pi$, arising from the concentration difference between two adjacent solutions, Δc . (b) Schematic depicting water electro-osmosis, in which the permeating ion (red circle) drags surrounding water molecules across the IEM. (c) Representative free volume factor, $\exp[-B_w(1-f_w)/f_w]$, as a function of fractional volume of water, f_w . (d) Schematic illustrating ion/uncharged solute selectivity, with dissolved diatomic gas, such as $H_{2(aq)}$, as the representative uncharged solute.

volume fraction in the membrane matrix (Geise et al., 2014b), i.e., $K_w \approx f_w$. If the solution and membrane are at equivalent hydrostatic pressures (bulk-phase solution is not pressurized and IEM is not under high swelling pressures, which are reasonable assumptions for most processes), the activities of water in the two phases are identical at equilibrium: $\gamma_w^s c_w^s = \gamma_w^m c_w^m$. Therefore, the activity coefficients, γ_w^s and γ_w^m , determine f_w and sorption of water into the IEM: $f_w \approx K_w = \gamma_w^s / \gamma_w^m$. Specifically, raising the activity coefficient of water in the IEM lowers the membrane affinity to sorb solvent. Mobility of solvent in the IEM is determined by the membrane structure and morphology. Using the free volume model, solvent diffusivity in the IEM can be expressed as a fraction, $\exp[-B_w(1-f_w)/f_w]$, of solvent diffusivity in bulk solution (Yasuda et al., 1968; Geise et al., 2014b). B_w is the characteristic parameter for water transport through

the free volume and is related to size of permeant, water. Therefore, reducing f_w hinders the mobility of water in the IEMs (Fig. 5(c)). Note that there are other transport theories to describe the mobility of water in IEMs (Liu and She, 2022), but essentially all approaches model smaller water mobilities for membranes with lower water volume fractions. As discussed earlier, ion transport is also influenced by f_w ; hence, altering solvent transport by changing f_w will inescapably also modify ion permeation and selectivity. This point will be further elaborated later in this subsection.

Because solvent molecules are almost always polar (e.g., water), charge-dipole interactions exist between the ions and solvent molecules. The migration of charged species within IEMs drags along surrounding solvent molecules, a phenomenon termed electro-osmosis (Spiegler, 1958; Strathmann, 2004). Part or all of the

solvation shell is transported along with the charged species, and neighboring solvent molecules (beyond the solvation shell) can also experience friction from the permeating species (Sata, 2004; Han et al., 2015). Electro-osmosis is commonly quantified by the number of solvent molecules transported along with one migrating ion (equivalent to electro-osmotic solvent flux divided by ion flux). To illustrate the range of transport, commercial IEMs exhibit electro-osmosis of 2.5, 6, and 8 for $\text{H}_2\text{O}/\text{H}^+$, Na^+ , and Cl^- , respectively (Nafion, Neosepta CMX, and Neosepta AMX) (Ren and Gottesfeld, 2001; Han et al., 2015). For IEM processes with multiple counterions or counter- and co-ions moving in opposite directions, electro-osmotic water flux, $J_{w, \text{eo}}$, is the net solvent transport from all the migrating species (subscript eo denotes electro-osmosis).

Osmotic permeance coefficient, $A_{w, \text{os}}$, scales with $\exp[-B_w(1 - f_w)/f_w]f_w(1 - f_w)^{-1}$ (product of migration and sorption, with factor $(1 - f_w)^{-1}$ accounting for convective frame of reference), suggesting that osmosis can be lowered by confining the amount of water in the membrane matrix or, equivalently, excluding water by raising γ_w^m (as $f_w \propto (\gamma_w^m)^{-1}$). Strategies to do so include altering the membrane chemistry to reduce the sorption of solvent (such as increasing the IEM hydrophobicity to lower water uptake), and crosslinking the polymer matrix or embedding a mesh substrate to structurally restrict membrane swelling by solvent (Paul et al., 2008; Porada et al., 2018; Rommerskirchen et al., 2021; Vlasov et al., 2022). Reductions in osmotic water flux as high as $\sim 60\%$ were demonstrated through limiting f_w (Paul et al., 2008). Because the driving mechanism is drag exerted by migrating ions, electro-osmosis remains generally independent of IEM properties, and reduced electro-osmosis is only observed for membranes that can maintain sufficiently solvent-poor environments (Tanaka, 2003). For example, the number of water molecules transported per ion remained invariant at ~ 4.1 but dipped to ~ 3.0 when the membrane was sufficiently solvent-poor (signified by low $A_{w, \text{os}}$) (Tanaka, 2003). The reduced electro-osmosis can be explained by the width of aqueous ionic channels falling below the size of the migrating ion-solvent clusters (a few nanometers or smaller) at such low water volume fractions, thus excluding solvent molecules usually drawn along by the charged species (Kreuer et al., 2004). Control of the phase separation during membrane fabrication by tuning the hydrophobic and hydrophilic groups of the polymer has been proposed as a potential approach to affect the nanoscale morphology of IEMs and restrain electro-osmosis (Kreuer and Münchinger, 2021). Inorganic membranes with rigid lattice structures, rather than conventional polymeric IEMs with flexible chains, show encouraging promise to eliminate water transport, with a recent study demonstrating virtually total suppression of both osmosis and electro-osmosis using NASICON membranes (Kim et al., 2022b). The complete

exclusion of water is attributed to the dimensions of the interstitial sites of the NASICON crystal structure being small enough to reject water molecules of 2.75 \AA (i.e., equivalent to $B_w \rightarrow \infty$ in the free volume model) but still able to accommodate bare Na^+ of $\sim 2.2 \text{ \AA}$, i.e., sodium ions dehydrate to enter the membrane (Zou et al., 2020).

Limiting osmotic and electro-osmotic solvent transport through lowering f_w will, however, also reduce the ionic conductivities of conventional polymeric IEMs. Ion mobilities were observed to decline with lower f_w (Goswami et al., 2001; Knauth et al., 2021). As discussed earlier, the free volume theory states that absolute mobility, u_i^m , scales reciprocally with the exponential of the ratio between the minimum free volume occupied by ionic species i and the total membrane free volume (Yasuda et al., 1968; Yasuda et al., 1971; Luo et al., 2020). Thus, constricting f_w concomitantly impedes ion mobility at the same time the transport of water is restricted (Geise et al., 2014b). A similar trend is also predicted by other models to relate the spatial effects of membrane structure and morphology with the mobility of ions across IEMs, such as the obstruction theory where ions migrate through tortuous paths formed by the water phase of the membrane matrix (i.e., space occupied by the polymer is inaccessible) (Fan and Yip, 2019). Because solvent and ion transport are both influenced by f_w , approaches to curtail osmosis and electro-osmosis by regulating solvent uptake of the IEM will invariably yield compromised ionic conductivity, i.e., akin to a permeability-selectivity tradeoff. To minimize the undesired retardation in κ_i while suppressing solvent transport, a thin solvent-excluding layer can be introduced, for example, as a coating film on the main membrane (Rommerskirchen et al., 2021). The dense film depresses solvent transport by steric exclusion, with the concomitant impediment to ion transport kept minimal because of the low membrane thickness. IEMs with transport mechanisms based on different principles from conventional polymeric membranes, such as NASICON membranes, can potentially depart from such tradeoff relationships (Kim et al., 2022b). Because electro-osmosis is intrinsically tied to ion transport, eliminating solvent molecules that are dragged across the membrane with permeating ions will be technically more challenging than the inhibition of osmosis.

4.2 Ion/uncharged solute selectivity

Besides ion and solvent, uncharged solutes can be present in the bulk solutions (Fig. 5(d)). These uncharged species are unaffected by Donnan exclusion of the charged membrane and, like neutral solvent molecules, crossover can be adverse to the performance of IEM applications. In redox flow batteries, complexation can occur between cations and anions to form uncharged species. For example, in vanadium redox flow batteries, VO^{2+} can

associate with SO_4^{2-} to form the neutral VOSO_4^0 complex, which can then diffuse across the IEM down a concentration gradient, lowering the Coulombic efficiency of energy conversion (Kreuer and Münchinger, 2021). Likewise, crossover of dissolved bromine is deleterious to the performance of hydrogen/bromine redox flow batteries (Darling et al., 2016). The transport of uncharged solutes detrimentally affects the performance of bioelectrochemical systems. For example, in microbial fuel cells, oxygen crossover from the cathode chamber compromises the anaerobic environment needed for the anode chamber (Li et al., 2011; Bakonyi et al., 2018). Additionally, the retention of neutral organic substrates and metabolites in their respective chambers is also desired (Kim et al., 2007; Harnisch et al., 2009). Artificial photosynthesis, which mimics the natural process to produce hydrocarbons, primary alcohols, and carboxylic acids, utilizes an anion exchange membrane to shuttle carbonate and bicarbonate ions from the catholyte to the anolyte. Crossover of CO_2 reduction products can result in the re-oxidation of these compounds at the anode, reducing overall efficiency because of product loss, wasted energy, and complications in subsequent product purification (Dischinger et al., 2020; Krödel et al., 2020). Diffusion of dissolved hydrogen gas through the hydrated proton exchange membrane is problematic for water electrolyzers and, to a lesser extent, fuel cells (due to the typically lower pressure differentials). In water electrolyzers, H_2 that crossover to the anode side competes to be oxidized with the desired oxygen evolution reaction and poses flammability hazards when the gas mixes with the $\text{O}_{2(g)}$ product (safety limit is 4 v/v% H_2 in O_2) (Bragg et al., 1994). In IEM bioreactors for wastewater treatment, ethanol dosed into the denitrification compartment and other uncharged carbon sources can diffuse across anion exchange membranes, causing secondary pollution of the treated stream (Fonseca et al., 2000; Matos et al., 2006; Matos et al., 2008). As such, the suppression of uncharged solute crossover is crucial for the advancement of these technologies.

Transport and retention of uncharged species are generally similar to neutral solvent molecules discussed earlier. Likewise, as the driving forces are different for ion and uncharged solute, discussion will focus on transport of the neutral species rather than S_{ij} . A key difference from solvent crossover is the diversity of uncharged species and, correspondingly, widely disparate solute properties. For example, $\text{H}_{2(aq)}$, VOSO_4^0 , and ethanol (crossover species of concern for electrolyzer, vanadium redox flow battery, and IEM bioreactor, respectively) have distinctly unlike sizes, diffusivities, and interactions with the polymer matrix. Additionally, among the different selectivities discussed here, ion/uncharged solutes selectivity and also the transport of neutral solutes across IEMs are the least studied topics.

For gaps in the current knowledge, we, therefore, look toward other membrane topics (e.g., reverse osmosis and nanofiltration). And like the other selectivities, efforts to suppress transport of the uncharged species are usually accompanied by a drop in ionic conductivity of the target ion (a nominal permeability-selectivity tradeoff). The following discussions will sequentially address the above-mentioned points.

Sorption of an uncharged species into the membrane is determined by the activity coefficients of the solute, $K_s = \gamma_s^s / \gamma_s^m$, with subscript s denoting solute (for membranes and bulk solutions at the same hydrostatic pressure). Hence, uncharged solute sorption can be reduced by raising γ_s^m . Tuning the hydrophilicity/phobicity of the membrane matrix has been shown to influence solute partitioning behavior for reverse osmosis and nanofiltration membranes, with more polar compounds exhibiting lower sorption into more hydrophobic membranes and vice versa (Ben-David et al., 2006a; Ben-David et al., 2006b). This approach can potentially be applied to modify the polymer backbone of IEMs, particularly for membranes with low water contents approaching those of reverse osmosis and nanofiltration membranes. At such low f_w^s , the role of solute-membrane interactions is relatively more significant, and the effects of exclusion are likely to be more pronounced.

Flux of the uncharged solute can be described by the classic convection-diffusion or, more correctly, advection-diffusion, equation (1st and 3rd terms of Eq. (3)). Because the solutions abutting the IEM are typically of different compositions, the transmembrane concentration gradient drives the diffusional flux of the uncharged species. In processes with significant pressure differentials across the membrane, e.g., pressurized cathode chamber in water electrolyzers, transmembrane concentration gradient of the uncharged species ($\text{H}_{2(aq)}$ in the example) is further amplified by the ΔP (Henry's law). Additionally, when there is solvent flux across the IEM (as discussed in the preceding section), advective transport of neutral solutes can be brought about by the fluid flow.

Steric hindrance was shown to be a primary factor affecting the transport of neutral organic solutes in conventional polymeric IEMs, with compounds of higher molecular weight having lower diffusive fluxes (Yasuda et al., 1968; Han et al., 2016). This is consistent with the free volume model for permeant transport discussed in the preceding sections, where permeant mobility scales with $\exp[-B_s(1 - f_w)/f_w]$. The characteristic parameter B_s is related to size of the permeant, with larger compounds having higher B_s s and, thus, more diminished mobilities (Yasuda et al., 1968; Amsden, 1998). Therefore, manipulating the transport channel widths can, in principle, increase steric exclusion of uncharged species, particularly solutes that are considerably larger than the

permeating ions. The alternative approach of lowering f_w can reduce the mobility of uncharged permeants, but would also concomitantly decrease conductivity of the desired ion. To limit the crossover of $H_{2(aq)}$ in water electrolyzers, proton exchange membranes above a certain thickness are used (typically ≈ 100 – $200\ \mu m$) (Trinke et al., 2019). While diffusion of $H_{2(aq)}$ is slower across thicker membranes, ion flux will also be proportionally depressed. The free volume model works reasonably well for neutral solutes with relatively high molecule weights and high swelling degree IEMs, suggesting that the permeants indeed transport through the solvated fraction of the membranes (Yasuda et al., 1969; Kato et al., 1992; Dischinger et al., 2020; Kim and Beckingham, 2021; Kim et al., 2021a; Kim et al., 2022a). However, for smaller solutes, such as $H_{2(aq)}$, and low swelling degree membranes, the permeant can plausibly be transported through the unsolvated free volumes within the polymer chains, akin to gas permeation across dense films (Baker, 2012). The exact mechanism of transport in that regime is yet to be conclusively established. Approaches investigated for the enhancement of other selectivities, such as NASICON, dense coating layers, and porous metal-organic frameworks, can potentially also improve the selectivity between ion and uncharged solutes, and warrant further studies. Lastly, reducing solvent flux would correspondingly lower the advective transport of dissolved neutral species. The understanding of transport (and retention) of neutral solutes in other aqueous separation membranes has made significant strides in the past decade (Marchetti et al., 2014; Wang et al., 2014a; Kingsbury et al., 2020; Wang and Lin, 2021). IEM studies can rapidly catch-up by drawing from these adjacent reservoirs of knowledge, to inform the development of membranes with improved exclusion of uncharged species.

5 Outlook and perspectives

Since the emergence of IEMs in the 1920s, continual improvements in charge selectivity for counterions over co-ions have enabled mainstream application of the membranes in industrial processes, most notably in the chloralkali process for chlorine and caustic soda production, and electrodialysis for brackish water desalination and ultrapure water demineralization (Sata, 2004; Strathmann, 2004). Almost all applications are, however, confined to bulk electrolyte concentrations $< 1.0\ eq/L$ because Donnan exclusion is diminished beyond those ion concentrations and charge selectivities of current IEMs are significantly compromised (Zlotorowicz et al., 2017; Fan and Yip, 2019; Kingsbury and Coronell, 2021). For applications that utilize electrolyte concentrations $> 1.0\ eq/L$, such as the chloralkali process, the detrimental impacts of co-ion leakage on performance

are significant. The frontier of charge selectivity is, thus, maintaining adequately high permselectivities even at high electrolyte concentrations. Doing so will extend the operating range of IEMs with better cost-effectiveness and energy-efficiencies. Valence selective IEMs are commercially available, specifically membranes that preferentially transport monovalent counterions over higher valence species. The further development of IEMs with improved valence selectivities, higher ionic conductivities with comparable selectivities, or preferential transport of higher valence counterions will enable the membranes to access new applications currently underserved by existing separation technologies. The selectivities achievable by nanofiltration membranes for ions with different valences ranges from ≈ 100 – 1000 (Wen et al., 2016; Abraham et al., 2017; Wang et al., 2018; Xi et al., 2018), suggesting that there is much room for improvements in current IEMs. Specific ion selectivity, in contrast, is in the incipient stages of development, with no existing commercial products marketed explicitly for such capability. Without charge as a differentiating feature and further compounded by the general similarities of other ion properties, such as solvated size, it is unsurprising that high selectivities for specific ions are technically challenging to attain. Encouragingly, current research in this area is vibrant. Here, and also in valence selectivity, innovations in materials offer prospects to utilize ion discrimination mechanisms that differ radically from conventional IEMs (Sheng et al., 2014; Li et al., 2020; Qian et al., 2020; Kim et al., 2022b; Xin et al., 2022), potentially allowing step-change improvements over current state-of-the-practice.

Ion/solvent and ion/uncharged solute selectivities are relatively underdeveloped compared to the ion/ion selectivities. The absence of common metrics to quantify the selectivities exemplifies this status. The introduction of standardized parameters to describe selectivity performance will, hence, be elemental to allow for comparisons and benchmarking. While it is recognized that solvent crossover is problematic for certain applications and has been well studied, there are currently no commercial IEMs tailored to suppress solvent transport. It is worthwhile to note that the driving force for solvent osmosis is different from ion electromigration (osmotic pressure and electrostatic potential differences, respectively), potentially presenting opportunities to suppress the former while sufficiently maintaining the latter for enhanced ion/solvent selectivity. Electro-osmotic solvent transport, on the hand, is intrinsically coupled to ion flux. Thus, more sophisticated strategies that uncouple the transport of ion and solvent will likely be needed. Again, material innovations hold promise to overcome this challenge (Kim et al., 2022b). Like solvent molecules, uncharged species are not affected by electrostatic potentials; therefore, their transport can potentially be isolated from the target ion. However, the

smaller size of many neutral species compared to solvated ions will likely frustrate steric exclusion approaches, leaving the utilization of unfavorable solute-membrane interactions as the primary option to lower solute sorption and enhance ion/uncharged solute selectivity.

Advancing fundamental understanding of the transport phenomena of ion, solvent, and uncharged species, specifically the governing mechanisms underpinning structure-property-performance relationships, will be vital for the informed development of more selective membranes. In this aspect, charge selectivity, the primary separation function of IEMs, is unsurprisingly the most established (Zlotorowicz et al., 2017; Fan and Yip, 2019; Kingsbury and Coronell, 2021), while recent studies have made progress in elucidating the factors governing valence selectivity (Ge et al., 2017; Chen et al., 2020; Fan et al., 2022). The formulation of rigorous first principles-based frameworks that quantitatively relate the membrane structure to sorption and migration properties, specifically membrane activity coefficients, γ^m , and absolute ion mobilities, u^m , and ultimately model separation performance will be vital to guide the rational design of IEMs with enhanced selectivities. This knowledge may be particularly pertinent for enhanced discriminations between specific ions, ion/solvents, and ion/uncharged solutes, for which fundamental understanding is less established. Here, future investigations can draw from other membrane disciplines and material science in general. For example, transport of water, other solvents, and neutral solutes have been extensively studied in reverse osmosis, nanofiltration, forward osmosis, and pervaporation (including applications of the techniques for organic solvents) (Silva et al., 2005; Cath et al., 2006; Shao and Huang, 2007; Vandezande et al., 2008; Marchetti and Livingston, 2015; Koh et al., 2016; Ismail and Matsuura, 2018; Song et al., 2019). Computational simulations of ion and molecule transports can be a helpful tool to understand nanoscale interactions not readily accessible through solely experimental means (Devanathan et al., 2007; Bedrov et al., 2008; Sun et al., 2014; Chen et al., 2018; Karal et al., 2020). Similarly, tapping into the highly promising potential of machine learning can complement experimental and simulation approaches and aid in the design of new membranes (Barnett et al., 2020; Fetanat et al., 2021; Ritt et al., 2022).

Recent studies indicate that approaches to improve sorption selectivity through preferential interactions, i.e., higher interaction free energies, will simultaneously have a retarding effect on mobility of the target ion (Zofchak et al., 2022). When the interactions are excessively strong, the target species can be immobilized, and the resulting material effectively behaves as an ion exchanger (Uliana et al., 2021). Consequently, efforts that utilize such approaches will need to navigate the inherently intertwined relationship and balance between the

concomitant changes to the sorption and migration of multiple permeating species. Instead of pursuing preferential affinity for the target ion, separation selectivity between two permeants can be attained by excluding the undesired species. Such a diametrically opposite strategy can, in principle, completely obstruct transport of the undesired species while sidestepping or partially mitigating the diminished mobility of the target ion, if highly precise control of the exclusion is achieved.

As discussed throughout this article, the tradeoff between permeability and selectivity appears to be pervasive. For high-value IEM processes (e.g., segregation of lanthanide ions), the benefits of more precise separations may outweigh the costs of lower ionic conductivities (such as larger membrane area requirements and greater energy demands). Conversely, other applications would likely need to be cost-competitive with existing methods and, thus, demand reasonably high permeabilities. Almost all the enhanced selectivities reported in the studies mentioned here came at the expense of reduced permeability, albeit to different extents. To advance these innovations to practical implementation, future efforts will need to restore some of the ionic conductivity. Reducing thickness of the selective layer or applying the selective layer as a coating film can be a way forward to improve permeability independently of selectivity, as shortening the transport pathway compensates for the lowered ion mobility but does not affect sorption (Chaudhury et al., 2014; Fan and Yip, 2019; DuChanois et al., 2022). Here, the technical challenge would be scaling up the manufacturing of module-sized membrane sheets that are integral and defect-free. Similarly, it remains to be seen if the sophisticated fabrication protocols employed in some of the bench-scale studies can be viably adapted to industrial-scale production. While past studies have demonstrated improvements in membrane selectivities over conventional IEMs, the target selectivity required for the intended application is seldom discussed. Defining the selectivities or, more accurately, the combinations of selectivities and ion permeabilities needed to realize practical implementation of emergent and emerging processes will more clearly identify the gap from current state-of-the-art and guide the charting of technological pathways forward.

Nomenclature

Acronyms

AEM	anion exchange membrane
CEM	cation exchange membrane
IEM	ion-exchange membrane
NASICON	Na super ionic conductor

Symbols

c	ion concentration
Δc^m	concentration difference across membrane
e	elementary charge
f_w	water volume fraction
k_B	Boltzmann constant
Δl	membrane thickness
t	transport number
u	mobility
v	velocity of water in membrane
z	ion valence
A	osmotic water permeability coefficient
B_w	characteristic parameter for water transport
B_s	characteristic parameter for solute transport
D	diffusivity
ΔE_i	binding free energy
F	Faraday constant
ΔG_{hyd}	Gibbs hydration energy
J	flux
K	sorption coefficient
ΔP	hydrostatic pressure difference across membrane
R	gas constant
S	separation selectivity
T	absolute temperature
γ	activity coefficient
ε	permittivity
κ	ionic conductivity
$\Delta \pi$	osmotic pressure difference across membrane
ϕ	electric potential
$\Delta \phi_D$	Donnan potential
$\Delta \phi^m$	electric potential difference within membrane

Superscripts and subscripts

ct	counterion
co	co-ion
eo	electro-osmosis
fix	membrane fixed charges
i	species i
j	species j
m	membrane phase
os	osmosis
s	bulk solution phase
w	water
l	upstream solution-membrane interface

2	downstream solution-membrane interface
I	monovalent counterion
II	divalent counterion
III	trivalent counterion

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