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## Review

## Monovalent cation perm-selective membranes (MCPMs): New developments and perspectives☆

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## ABSTRACT

As one of the most typical and promising membrane processes, electrodialysis (ED) technique plays a more and more significant role in industrial separation. Especially, the separation of monovalent cations and multivalent cations is currently a hot topic, which is not only desirable for many industries but also challenging for academic explorations. The main aim of the present contribution is to view the advances of a wide variety of monovalent cation perm-selective membranes (MCPMs) and their preparation technologies including (1) covalent cross-linking, (2) surface modification, (3) polymer blending, (4) electrospinning, (5) nanofiltration alike membrane, and (6) organic–inorganic hybrid. The relevant advantages and disadvantages with respect to some specific cases have been discussed and compared in detail. Furthermore, we elaborately discuss the opportunities and challenges of MCPMs, the fabricating strategies to take and the future perspectives.

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## 1. Introduction

Ion exchange membranes (IEMs) are typically composed of hydrophobic polymer matrix, immobile charged ion exchange groups, and movable counter-ions. Since last century, IEMs as emerging materials for ion separation, have drawn significant attentions due to their wide applications in seawater desalination [1], environmental protection [2], resources recovery [3] and energy production [4]. The extensive applications of IEMs further promote the investigations in both academic and industrial level. Meanwhile, new essential properties of traditional IEMs are proposed to satisfy the specific applications, e.g., electrodialytic concentration of seawater to produce sodium chloride [5], acid recovery in hydrometallurgy [6], removal of specific ions in liquid waste [7], and lithium recovery from brine [8,9]. One of the general issues in the above-mentioned systems is the presence of monovalent cations and multivalent cations. In this case, perm-selective permeation of monovalent ions through the membranes is indeed needed. Thereby, more efforts have been devoted towards the preparation of cation exchange membranes with perm-selectivity for monovalent cations [5,10–18].

As the name suggests, monovalent cation perm-selective membranes (MCPMs) allow the high permeation of monovalent cations, while retaining the selective passage of multivalent cations [19]. Owing to the distinguished functions, MCPMs have been extensively investigated in different applications. Specifically, in this review the topics are mainly focused on electrodialysis (ED) and diffusional dialysis (DD) processes, although there are many other fields concerned with ionic separation/fractionation [17,20–22].

## 2. Mechanism of the Perm-selective Separation of MCPMs

Perm-selectivity of cations in a mixture through MCPMs is basically governed by their affinity towards the membranes (ion exchange equilibrium constant) and the migration speed in the membrane phase (mobility ratio among the cations) [12,13,19]. Based on this universal rule, various mechanisms have been proposed to explain the perm-selective separation of the MCPMs, which were summed up as follows: (1) pore-size sieving effect decided by the different hydrated ionic radii, (2) electrostatic barrier effect due to the difference in electrostatic repulsion between monovalent cations and multivalent cations, and (3) hydration energy difference caused by the different Gibbs hydration energy of cations.

To simplify the system,  $\text{Na}^+$  ion is generally used as a standard cation. When one equivalent of  $\text{Na}^+$  ion permeates through MCPMs, the permeated equivalency of a given cation is evaluated.

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Perm-selectivity between cations A and  $\text{Na}^+$  ion is represented as  $P_{\text{Na}^+}^A$ , which is called as relative transport number ratio of cations A to  $\text{Na}^+$ , and is defined by the following equation [23],

$$P_{\text{Na}^+}^A = \frac{(t_A/t_{\text{Na}^+})}{(C_A/C_{\text{Na}^+})} \quad (1)$$

where,  $t_A$  and  $t_{\text{Na}^+}$  are the transport numbers of cations A and  $\text{Na}^+$  in the membrane phase, whereas  $C_A$  and  $C_{\text{Na}^+}$  show the concentration of cations A and  $\text{Na}^+$  at the surface of membrane on desalting side of solution during electrodialysis, respectively. In fact, in order to calculate simply, the reported perm-selectivity in some studies is directly considered as the flux ratios of  $\text{Na}^+$  ion and cation A, especially when the feed solution contains equal concentrations of the two ions [24–26].

### 3. Traditional Technologies for Fabricating MCPMs

#### 3.1. Covalent cross-linking

Perm-selective separation by pore-size sieving effect based on the polymeric network is firstly proposed according to the difference in hydrated ionic radius of ions. It is believed that covalent cross-linking technique is a promising way of improving both the compactness and chemical stability of MCPMs. The improved compactness of the membrane would lower the migration speed of cations and the ions with smaller hydrated ionic radii would easily pass through the membrane. For example, polycondensation of phenolsulfonate-phenol-formaldehyde system [27] or sulfonation of copolymer membranes composed of styrene and divinylbenzene (DVB) [28] was adopted to fabricate MCPMs. The perm-selectivity increased remarkably with the content of cross-linking agent, which caused a decreasing pore size of the membranes. Specifically, the higher perm-selectivity was usually observed in the condensation-type membranes as compared to the copolymerization-type membranes. That is because ion exchange equilibrium constant of divalent cations to monovalent ions greatly increases — in the condensation-type membranes in contrast to the slight decrease in the copolymerization-type membranes [27]. Sol-gel process under acidic condition is known as another approach to prepare MCPMs [29]. The inorganic segment (silica) inside the poly(vinyl alcohol) matrix led to a more compact membrane structure, it was thereby very difficult for the bulkier cations to pass through, resulting in a high perm-selectivity, especially for  $\text{Na}^+/\text{Fe}^{3+}$  system (the perm-selectivity was approximately equal to 10). Generally, the covalent cross-linking strategy often improves the compactness of membranes which affects the migration speed of cations in the membrane phase, and it thus obtains an enhanced perm-selectivity. While it can be seen that high cross-linking would cause high electrical resistance that is not desirable for the practical ED application [30,31].

#### 3.2. Surface modification

Surface modification is adopted to decrease the electrical resistance and maintain monovalent ion perm-selectivity simultaneously by tailoring the surface properties of the membranes. Unlike covalent cross-linking structure in membrane matrix, in this way, only the membrane surface is decorated by a functional layer, and it is thus expected to obtain high ionic flux and low electrical resistance. The modification techniques can be divided into two categories: surface physicochemical modification and covalently chemical modification.

##### 3.2.1. Surface physicochemical modification

The physicochemical modification includes surface polymerization [32,33], direct coating [34,35], electrodeposition [36,37], and layer-by-layer self-assembly [14,25]. Here, examples of the reported surface modified membranes have been taken to illustrate the versatility of the physicochemical modification. To produce a compact polymer layer by polymerizing monomers *e.g.* pyrrole, aniline and dopamine on the membrane surface is a very typical method among them. Such polymerization technique is facile and the polymer layer shows good adjustability and affinity to the IEM matrix [16,38–40]. The modified layer brings hydrophilic nature and different charge density from functional groups, which leads to adjusted surface compactness, contact angle, conductivity and perm-selectivity. For example, Gohil *et al.* [38] developed MCPMs with a polypyrrole layer. The dialysis rate decreased in the sequence of  $\text{NaCl} > \text{CaCl}_2 > \text{MgCl}_2 > \text{CuCl}_2$  and relative dialysis rates of  $\text{NaCl}$  with respect to different divalent electrolyte were varied between 5 and 8 in the use of mixed electrolytes, indicating the compact polypyrrole layer on the membrane surface could serve as a rejection layer for the migration of bulky ions, and the efficient separation of mono-/di-valent electrolyte was achieved. In fact, a compact layer on the membrane surface, no matter a polymer layer or an inorganic layer, is beneficial to strengthen the pore-size sieving effect and improve the perm-selectivity. Recently, a novel modification method through controllable metal loading on the surface of poly(2-acrylamido-2-methyl-propane-sulfonic acid) (PMPS) membranes by an electro-less plating technique was proposed by Thakur *et al.* (Fig. 1) [41]. The metal loading on the membrane surface could form a thin rigid layer, and it partially inhibited the ionic transport of bulkier cations. Due to the improved surface compactness, the flux ratio between  $\text{Na}^+$  and  $\text{Ni}^{2+}/\text{Zn}^{2+}$  was significantly increased up to  $\sim 100$ . The membranes exhibited excellent monovalent cation perm-selectivity without any significant deterioration in  $\text{Na}^+$  transport. This work provides a new sight on fine tuning perm-selectivity and ionic flux of the CEM by constructing a thin metallic layer.

In addition, Farrokhzad *et al.* [15] prepared PCMPs by decorating polyaniline (PANI) on sulfonated CEM surface with different doping agent. The dense PANI layer had a lower charge density than the pristine membrane and it hindered the migration of  $\text{Mg}^{2+}$  ions through the

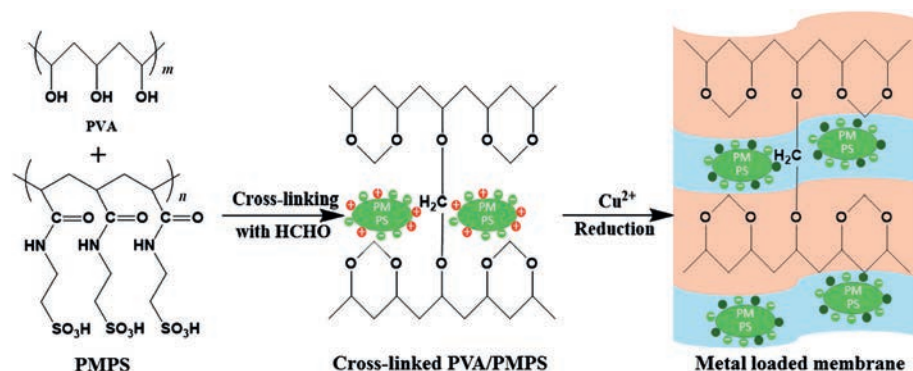


Fig. 1. Preparation of the metal loaded PMPS membrane. (Reproduced from Ref. [41].)

membrane compared to  $\text{Na}^+$  ions. In addition, the different hydrophilicity of the membrane surface caused by different doping agent would also affect the transport behaviors of the cations resulting from the different hydration energy of cations. The composite membrane coated by PANI–pTSA (para-toluene sulfonic acid) exhibited a very high selectivity for monovalent ions ( $\sim 7.1$ ). The hydrophilic surface actually facilitated the transport of  $\text{Mg}^{2+}$  ions and the hydrophobic surface led to the easier diffusion of  $\text{Na}^+$  ions, resulting from the energy barrier of partial ion dehydration [42,43]. These results clearly reveal that the perm-selectivity is determined by the hydrated ionic size and the water affinity (the Gibbs hydration energy) of cations [44,45].

Rodzic [46] modified cation exchange membranes (CEMs) surface by two different methods viz. electrodepositing and coating aqueous chitosan hydrochloride, it was found that the introduction of chitosan layer boosted the perm-selectivity of the membranes obviously. A higher perm-selectivity of  $\text{Na}^+$  over  $\text{Mg}^{2+}$  could be observed by increasing the thickness of chitosan layer via increasing electrolyte concentration, applied current density and sorption time. Importantly, the authors claimed that apart from the pore-size sieving effect, the electrostatic barrier effect of the chitosan layer should also be taken into account in evaluation of membrane perm-selectivity.

In fact, some other studies also reported that multivalent cations were difficult to adsorb in anion exchange membranes (AEMs) as compared to monovalent cations, because of the difference in the electrostatic repulsion between the relevant cations and the membranes [47]. In view of this, Amara and Kerdjoudj [48] prepared MCPMs by immersion and electrodeposition methods to adsorb highly protonated polyethyleneimine (PEI), the perm-selectivity of the membrane increased due to the strong repulsion effects of protonated PEI multilayers to divalent ions. Notably, PEI here was an effective carrier for proton via the acid–base reaction between ammonium and amine groups, which facilitated the transport of  $\text{H}^+$  ions and thus improved the perm-selectivity of  $\text{H}^+$ /metallic ions. Hu *et al.* [49] reported that electrodepositing quaternized chitosan layer improved the monovalent ion selectivity of the base membrane. After the formation of quaternized chitosan layer,  $\text{Zn}^{2+}$  leakage dropped abruptly from 9.36% to 1.035% and  $\text{Al}^{3+}$  leakage declined from 7.75% to 0.83%, which could be attributed to the electrostatic repulsion between metallic ions and cationic layer during the selective separation process of  $\text{H}^+$  ions from multivalent cations. In summary, positively charged ion exchange groups are desirable to the CEMs in order to permeate preferentially monovalent cations rather than multivalent cations. However, it is noted that the electrodeposition or immersion method leads to monolayer adsorption of polyelectrolyte, the improvement of the perm-selectivity is still limited.

Recently, a layer-by-layer (LBL) polyelectrolyte deposition method is employed to enhance the perm-selectivity of IEMs by producing ultrathin coating on the membrane surface, an ultrathin multilayer could be achieved by an alternating adsorption of polycations and polyanions [14,17,50–53]. The high charge density may induce the enhanced electrostatic interaction and size-based exclusion of highly hydrated ions, and it thereby improves the perm-selectivity of the membranes. For example, Cheng *et al.* applied LBL technique to prepare 5-bilayer poly(sodium 4-styrene sulfonate) (PSS) and protonated poly(allylamine hydrochloride) (PAH) films on a nanofiltration membrane or porous alumina membrane, the selectivity for  $\text{K}^+/\text{Mg}^{2+}$  could be as high as  $\sim 100$ . However, the uncharged membrane substrates caused low transference numbers of the LBL modified membranes, which limited their utility in ED process that required transport of only cations or anions through a membrane [54]. To eliminate these defects, positively charged Nafion 115 membrane was used as a substrate for the preparation of MCPMs by LBL technique. Remarkably, the  $\text{K}^+/\text{Mg}^{2+}$  selectivity values were more than 1000 as the current density was at or below  $1.59 \text{ mA} \cdot \text{cm}^{-2}$  (Fig. 2) [24]. The high perm-selectivity was actually originated from the large hydrated ionic radius and electrostatic repulsion force of multivalent ions [18]. These findings are expected to direct the design of MCPMs for mono-/multi-valent cation separation in ED process.

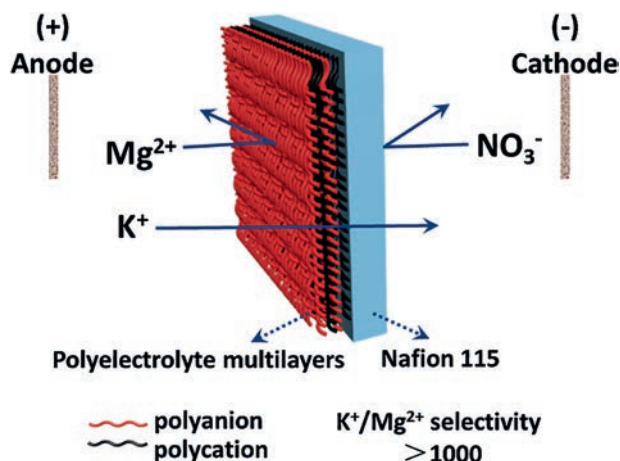


Fig. 2. Coating of CEM with a polyelectrolyte multilayer to achieve high  $\text{K}^+/\text{Mg}^{2+}$  perm-selectivity.  
(Reproduced from Ref. [24].)

To date, the perm-selective ion separation of LBL modified membranes still remains a big challenge. A detailed and deep description of ion transport through the multilayer architectures is needed as the results from different studies are controversial [14]. In fact, parameters in LBL process such as the number of layers, thickness, compartment concentration, applied current density and boundary layer thickness play important roles in the final performance [18,24,25,54,55]. For example, when PEI/PSS multilayers as a perm-selective layer were coated on a Neosepta CMX membrane by LBL method, all the PEI/PSS modified membranes showed higher limited current density of approximately  $\sim 20 \text{ mA} \cdot \text{cm}^{-2}$  than that of PAH/PSS modified Nafion membranes [24,25], but, the  $\text{Na}^+/\text{Ca}^{2+}$  perm-selectivity was only 1.35, which was not so attractive.

Furthermore, the relatively weak physical interactions between ionic polyelectrolyte and ion exchange groups of the membrane would induce gradual decrease of perm-selectivity during a continuous operation process [56,57]. In conclusion, systematic researches on diversified parameters in LBL process should be considered to investigate the mechanism on how the parameters affect the final performance of the membranes.

### 3.2.2. Surface chemical modification

As mentioned above, the long-term stability of modified layer of membranes in ED process still remains unsatisfactory. In these techniques, they only involve the physical interactions such as electrostatic attraction and intermolecular force between the modified layer and membrane matrix. In order to overcome this drawback, other approaches such as diazonium-induced anchoring process [58,59], photo-induced covalent immobilization [60] and the formation of a sulfonamide bond [61–63] have been proposed to form a stable connection between membrane matrix and the modified layer. For example, Chamoulaud and Belanger [64] converted sulfonic acid groups of a base membrane into  $-\text{SO}_2\text{Cl}$  groups which subsequently reacted with a diamine to create a sulfonamide bond and a tertiary amine terminal, and finally incorporated with methyl iodide or protonation to obtain a cationic layer on the membrane surface (Fig. 3). The ED results demonstrated a significant decrease in  $\text{Zn}^{2+}$  leakage from 6.8% to 0.3% because the cationic layer allowed the transport of  $\text{H}^+$  ions, but blocked the  $\text{Zn}^{2+}$  ions due to the electrostatic barrier. Li *et al.* [65] decorated chlorosulfonated groups on membrane surface to react with polyquaternium-7. Due to the electrostatic exclusion from the modified thin layer, an obvious decrease in the metal ions leakage ( $\text{Zn}^{2+}$  leakage decreased from 22.0% to 14.2%,  $\text{Ca}^{2+}$  leakage from 53.1% to 38.0% and  $\text{Mg}^{2+}$  leakage from 81.7% to 32.8%) could be observed. In addition,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  have the equal electrostatic force, the different final

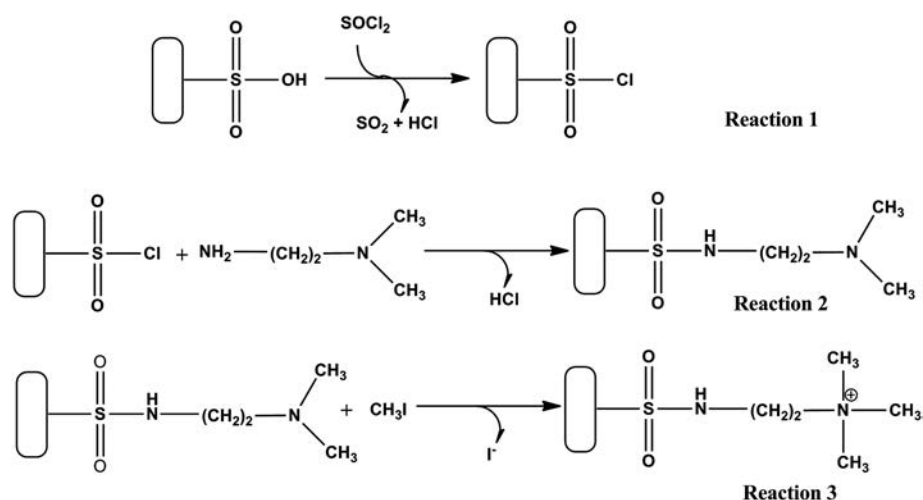


Fig. 3. Modification of the CEM by chlorosulfonation (Reaction 1), amination (Reaction 2), and quaternization (Reaction 3). (Reproduced from Ref. [64].)

perm-selectivity of  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ions suggested that the steric barrier played a more important role in perm-selectivity. However, these membranes exhibited good monovalent cation perm-selectivity and durability, and hazardous chemicals such as  $\text{SOCl}_2$  were used to prepare  $-\text{SO}_2\text{Cl}$  groups. Therefore a more effective diazonium-induced anchoring process (DIAP) was proposed by Le *et al.* [66], in which a thin “polyaniline-like” layer was inserted covalently on the surface of commercial CMV membrane through a one-step chemical process (Fig. 4). Compared with the pristine membrane, a great enhancement in perm-selectivity from 17.9 to 166.7 between  $\text{H}^+$  ions and  $\text{Ni}^{2+}$  ions was achieved. Most interestingly, the membrane resistance increased very slightly (about 8%) as the modified layer by DIAP was very thin. In another similar work [58], diazonium-induced carboxyl groups

were grafted on the membrane surface by covalent immobilization of PEI multilayer. The divalent cation leakage of the modified membranes was decreased remarkably ( $\text{Mg}^{2+}$  leakage from 7.1% to 0.4% and  $\text{Zn}^{2+}$  leakage from 2.1% to 0.55%) which was ascribed to the electrostatic force of repulsion between the cations and the attached positively charged PEI multilayer. Thus, this method shows superior advantages to other available chemical modification methods [53,56,60].

### 3.3. Polymer blending

As previously stated, the perm-selectivity is not only determined by the pore-size sieving effect and electrostatic repulsion, but also influenced by the Gibbs hydration energy of cations. Thus, it is available to

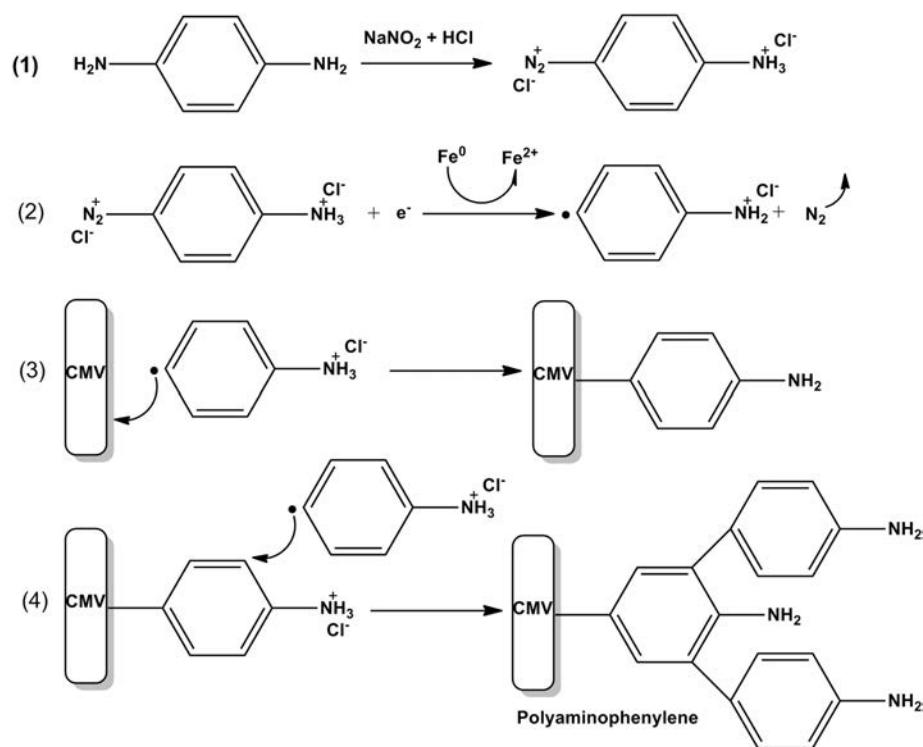


Fig. 4. Modification of CMV by DIAP: (1) diazotization, (2) reduction of the aryldiazonium groups, (3) grafting of the aryl radicals onto the surface, and (4) growing of PAP multilayer. (Reproduced from Ref. [66].)



tune the hydrophobicity and hydrophilicity of membranes to improve the perm-selectivity. Polymer blending is a very useful technique to fabricate MCPMs which combines the hydrophilic and hydrophobic characterizations of different polymers into a polymer hybrid, and thus improves the resulting stability, perm-selectivity and conductivity [67]. In such polymer hybrid, the hydrophilic polymer part creates plenty of constructed water channels which facilitate ion transport, meanwhile the hydrophobic polymer part can restrict the water swelling, as a result, improved perm-selectivity of IEMs can be obtained. The perm-selectivity is controlled by the different migration speed of the respective ions and affinity of the ions with the membrane [12,44]. A good modification procedure should balance the hydrophobicity and hydrophilicity of membranes because too many hydrophilic groups would cause perm-selective failure. Some studies tried to adjust the ratio of hydrophobic/hydrophilic groups in the membranes to optimize the interaction between ions and membrane matrix. For example, Balster *et al.* [68] prepared MCPMs by blending hydrophilic sulfonated poly(ether ether ketone) (SPEEK) and hydrophobic poly(ether sulfone) (PES), the  $\text{Ca}^{2+}$  transport through the membrane was actually determined by the conductivity and the charge density of the membrane. In addition, blending of SPEEK with poly(arylene ether ketone) derivatives containing crown ether (CPAEK) induced significant increase of the  $\text{K}^+$  over  $\text{Li}^+$  selectivity by a factor of nearly 4 due to the tuned hydrophobicity of the blend membranes and the complexation interaction between  $\text{K}^+$  and the crown ether. It is believed that polymer blending is a versatile method either to tune the hydrophobicity and hydrophilicity of the blend membranes or introduce the specific complexing-forming groups in the membranes, which further adjusts the final ionic flux and perm-selectivity [69]. Moreover, simplicity is an obvious advantage of this method. However, to achieve a significantly improved perm-selectivity still remains a big challenge due to the limited inherent properties of the used polymers.

#### 4. Emerging Technologies for Manufacturing MCPMs

##### 4.1. Electro-spinning for constructing ionic channels

Electrospinning technique is an emerging technology for preparing polymeric fibers which can be used in the membrane preparation by further compressing procedure. For example, nanofibrous composite membranes were obtained by electrospinning quaternized poly(2,6-dimethyl-1,4-phenyleneoxide)/silicon dioxide hybrid material (QPPO-SiO<sub>2</sub>) followed by solvent fumigation and hot-press [70]. The resulting membranes possessed interconnected porous structure, large specific surface area and good flexibility to offer an ion conductive pathway, and exhibited desirable transport properties and enhanced structural stability. Both acid permeability ( $U_{\text{H}} = 0.053 \text{ m} \cdot \text{h}^{-1}$ ) and selectivity ( $S = 68.1$ ) of the nanofiber composite membranes increased as compared to solution-cast QPPO-SiO<sub>2</sub> membrane ( $U_{\text{H}} = 0.041 \text{ m} \cdot \text{h}^{-1}$

and  $S = 49.5$ ) for acid recovery during diffusion dialysis process. Chakrabarty *et al.* also reported the fabrication of electro-spun nanofibrous membranes composed of SPEEK for selective electro-transport of ions. The nanofibrous membranes exhibited very low flux and electro-transport efficiency of divalent cations, which showed a promise to purify brackish water into potable drinking water in the chloralkali industry [71]. Recently, our group developed a new method to tailor nanofibrous composite membranes containing  $-\text{N}^+(\text{CH}_3)_3$  and  $-\text{SO}_3^-$  groups by impregnating QPPO nanofibrous mats into sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) solution. Sulfonic groups of SPPO acted as continuous carriers for cations transmission while the quaternary ammonium groups played an important role in separating monovalent cations from divalent cations according to the electrostatic repulsion. As shown in Fig. 5, compared with the commercial monovalent cation selective membrane (CSO), the optimized membrane exhibited higher ionic flux of  $2.96 \times 10^{-8} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$  and the perm-selectivity of 1.62. Meanwhile, the unique structure resulted in lower electrical resistance, higher limited current density and significant improvement in dimensional stability [72].

##### 4.2. Nanofiltration alike membrane for electrodialysis (EDNF)

Traditionally, ion exchange membranes prepared by solvent evaporation method are dense ones. The dense structure limits the ion diffusion, ionic flux and high surface resistance as well. On the contrary, nanofiltration membranes and ultrafiltration membranes prepared by phase inversion technique are typically porous and they have relatively high flux. Therefore, it is reasonable to construct porous structures in ion exchange membranes would be expected to get high ionic flux and low surface resistance. Klayson *et al.* prepared porous cation exchange membranes by blending sulfonated SiO<sub>2</sub> mesoporous silica with sulfonated polyethersulfone *via* phase inversion technique. The porosity and pore size of the ion exchange membranes increased with increasing SiO<sub>2</sub> loading and thus significantly enhanced ionic conductivity and transport properties. The optimal membrane had a high transport number of 0.95 as well as good mechanical strength and thermal stability. Electrodialysis experiments showed that both the current efficiency and the energy efficiency could be comparable with the commercial ion exchange membrane. Sun *et al.* [73] used porous BPPO-based AEMs for acid recovery *via* diffusion dialysis. The porous morphology of the membrane conducted the decreasing ion transport resistance. The proton dialysis coefficients were in the range of 0.020 to  $0.025 \text{ m} \cdot \text{h}^{-1}$  at  $25^\circ\text{C}$ , whereas the separation factors appeared from 28.6 to 45.5. Both were higher than those of commercial dense DF-120 AEM ( $0.009 \text{ m} \cdot \text{h}^{-1}$  and 18). A similar work was conducted by our group in which charged porous membranes with tunable morphologies were prepared *via* NIPS technique for acid recovery. It could be seen that the finger-like structure provided higher dialysis coefficient of  $\text{H}^+$  but lower selectivity, while the sponge-like structure displayed outstanding

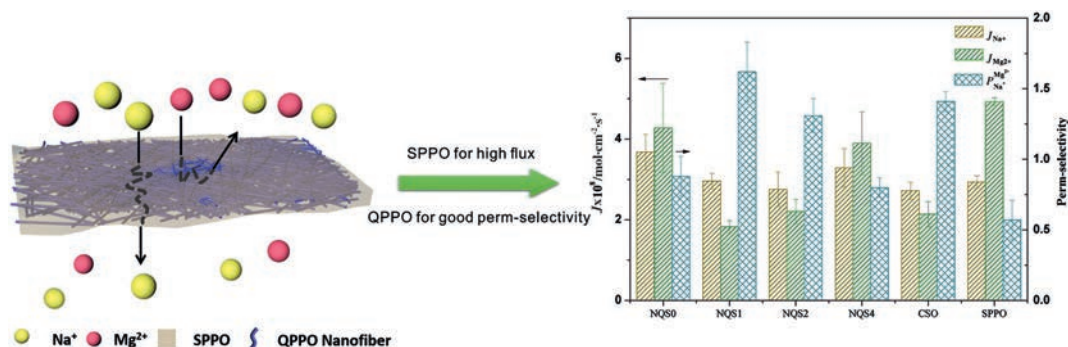


Fig. 5. Schematic transport of  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  through the nanofibrous composite membrane.

$H^+$  dialysis coefficients and separation factors. Specifically to the  $HCl/AlCl_3$  system, the separation factor reached as high as 2033 [74]. Inspired by these successful applications and excellent performances of porous ion exchange membranes in ED and DD process, it stands to reason that whether or not the porous membranes can conduce good performances for monovalent cation perm-selectivity separation.

Generally, a nanofiltration membrane has a porous bulk structure and a dense layer, the monovalent ions could pass through but the multivalent ions are blocked up under the pressure drop. While electrodialysis can allow the ion transport according to the charge, e.g. anions move towards anode through an AEM and *vice versa* for cations. Hence can we combine them into one membrane unit? i.e., can we use a nanofiltration-like membrane to separate selectively mono-/multivalent ions *via* electrodialysis? To verify this thinking, a nanofiltration-like membrane was prepared by non-solvent induced phase separation and interfacial polymerization and integrated with ED process for selective ion separation. As shown in Fig. 6A, in this process, the ions transfer through the nanofiltration-like membrane from one side to other side under an electric field, which can realize the concentration and desalination of the solution. The dense layer of nanofiltration-like membrane rejects the multivalent cations rather than the monovalent cations due to the different hydrated ionic radii of ions, leading to a high perm-selectivity of  $Na^+$  and  $Mg^{2+}$  ions. Furthermore, the porous structure of nanofiltration-like membrane can largely decrease the transfer resistance of ions and enhance the flux of monovalent ions. As a result, the  $H^+$  ion flux could reach to  $3.4 \times 10^{-7} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$  with the ion flux ratio of 354 for  $H^+/Zn^{2+}$  system (Fig. 6B) and achieve  $2.2 \times 10^{-7} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$  of  $Na^+$  ion flux with the ion flux ratio of 7 for  $Na^+/Mg^{2+}$  system (Fig. 6C) in this new process. Both of the perm-selectivity and ionic flux were higher than those of CSO membrane [26]. The results clearly demonstrate the superiority of EDNF process in which effective separation of monovalent cations from divalent

cations and desalination and concentration of solution are achieved simultaneously.

#### 4.3. Mixed matrix membranes (MMMs) by organic–inorganic hybrid

Mixed matrix membranes (MMMs) comprised of polymeric components and embedded inorganic particles are promising for designing high performance IEMs [75–77]. MMMs combine the advantages of both polymers (e.g. flexibility, adjustable IEC and processing ability) and inorganic particles (e.g. ion adsorption ability, thermal and mechanical stability). Generally, multi-phase MMMs can be prepared to manifest the desired properties of each component. In order to improve the monovalent ion perm-selectivity of IEMs, many inorganic particles (e.g.  $SiO_2$  nanoparticles [78], multi-walled carbon nanotubes [79], iron–nickel oxide nanoparticles [80] and  $Fe_3O_4$ /PAA core–shell nanoparticles [81]) are employed to cooperate into the polymer matrix. For example, Hosseini *et al.* [82] prepared polyvinylchloride-co- $TiO_2$  nanoparticle MMMs by solution casting technique. The prepared MMMs had a different transport behavior for  $Na^+$  ions and  $Ba^{2+}$  owing to the different  $TiO_2$  nanoparticle loading ratio. When the ions transferred across the MMMs, the ionic flux was affected by many factors including the adsorption ability of  $TiO_2$ , the formation of narrow channels by  $TiO_2$  as well as the decreased resin particles' accessibility *via* an isolating phenomenon. The iron–nickel oxide ( $Fe_2NiO_4$ ) nanoparticle was also used to fabricate MMMs for ion separation [80]. Interestingly, due to the good adsorption property of  $Fe_2NiO_4$  to  $Ba^{2+}$  ions, the ionic permeability and flux of  $Ba^{2+}$  ions increased with the increasing  $Fe_2NiO_4$  content, the MMMs showed higher perm-selectivity for divalent cations compared to monovalent cations. Apart from the above-mentioned works, our group proposed a graphene oxide (GO) embedded “three-phase” membrane composed of hydrophilic phase, hydrophobic phase and auxiliary phase (Fig. 7). For the auxiliary phase, the formation of

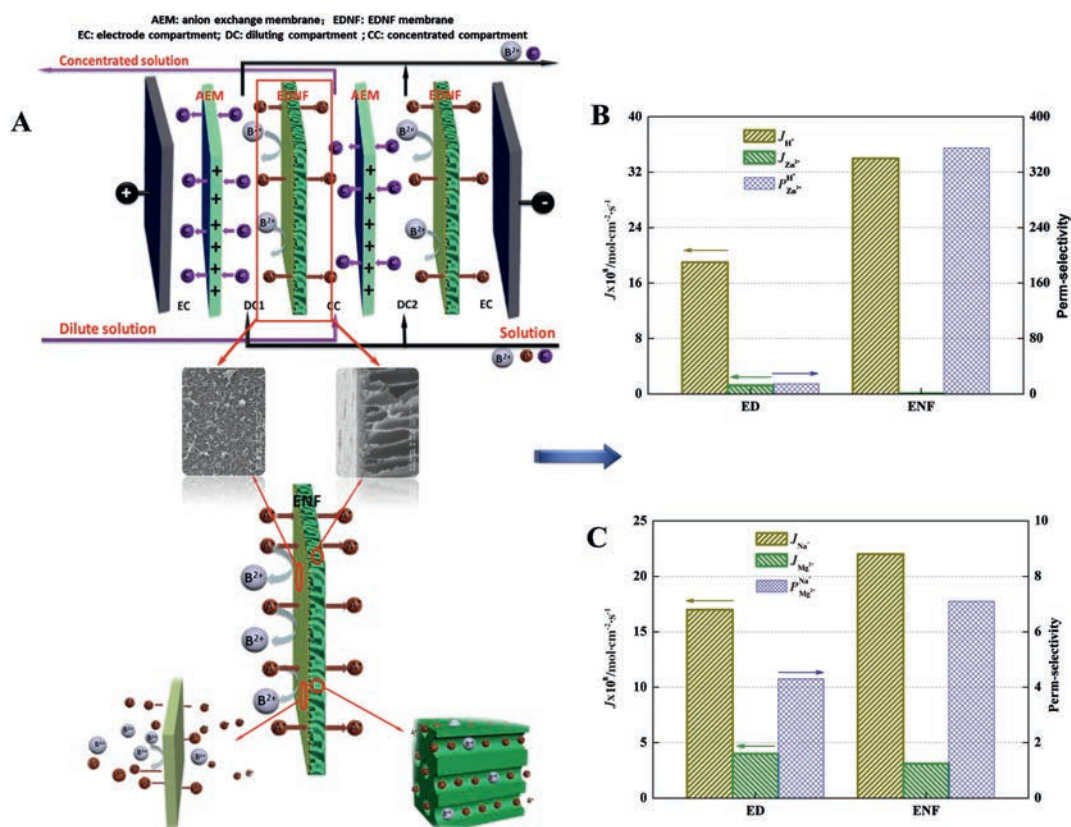


Fig. 6. Electrodialysis with nanofiltration membrane (EDNF) for high-efficiency cations fractionation.

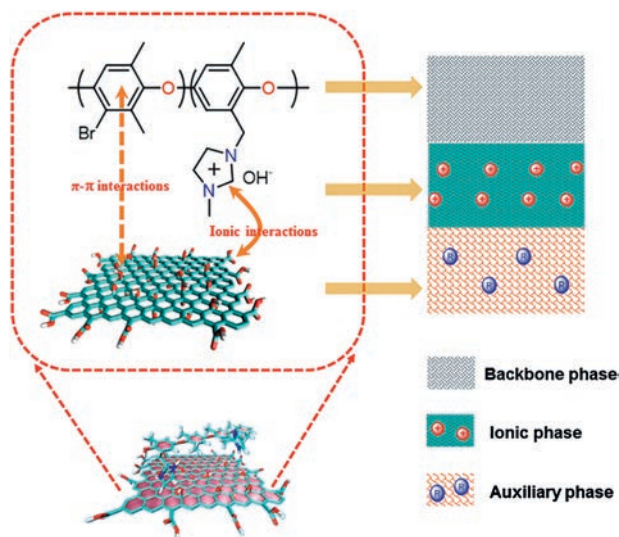


Fig. 7. Schematic procedure to synthesize the "three-phase" AEMs containing GO sheets.

hydrogen-bonding networks and the increase of the hydrophilicity led to more efficient transfer of  $\text{H}^+$  ions. Meanwhile, the strong adhesive force between  $\text{Fe}^{2+}$  ions and the oxygen-containing groups attached on the GO sheets' surfaces hindered the transport of  $\text{Fe}^{2+}$ . As a result, both acid permeability ( $U_{\text{H}} = 0.029 \text{ m} \cdot \text{h}^{-1}$ ) and selectivity ( $S = 115$ ) of the "three-phase" membranes increased as compared to "two-phase" membrane ( $U_{\text{H}} = 0.021 \text{ m} \cdot \text{h}^{-1}$  and  $S = 76$ ) for acid recovery via diffusion dialysis, indicating the introduction of added auxiliary phase successful beat the "trade-off" effect [83].

In general, the study of MMMs for ion separation is still at an infancy stage, more investigations should be carried out including the effect of the adsorption characterization, the size and dimensions, the shapes (layered, porous, and compact structures), and the dispersion of particles in polymer matrices on the ionic flux and perm-selectivity.

#### 4.4. Other technologies

Besides the above-mentioned technologies, some other technologies are available to endow the IEM perm-selectivity. As mentioned above, the additional cross-linking agents are adopted in some researches to improve the compactness of the membranes. However, for semi-crystalline polymeric ion exchange membrane, the annealing post-treatment is an alternative way of operating the crystallization process and thus improving the selectivity in various applications including

gas separation [84], vapor permeation [85] and ion-selective permeation [86,87]. Our group proposed an annealing procedure to adjust crystallinity and enhance crystalline domains in polyvinyl alcohol-based CEM, the as-obtained CEM exhibited improved pore-size sieving effect of ions. The larger Stokes radii of  $\text{Zn}^{2+}$  ions were much more difficult to transport through the dense membrane than the smaller  $\text{H}^+$ . The annealed membrane with a crystallinity of 43.9% exhibited a favorable perm-selectivity of 142.9 between  $\text{H}^+$  and  $\text{Zn}^{2+}$  and extremely low  $\text{Zn}^{2+}$  leakage of 0.01% [88]. Alternatively, constructing ion channels via acid–base interaction has been done by many researches in fuel cell membranes, which can also significantly improve the compactness of a membrane matrix [89–93]. In one of our works, we successfully constructed MCPMs through the formation of acid–base pairs of imidazole and sulfonic acid groups (Fig. 8). The hydrogen bonding networks integrated with the acid–base pairs enabled the denser membrane structure, which lowered the  $\text{Zn}^{2+}$  leakage compared with the pristine membrane. More importantly, this method induced micro-phase separation in membranes and the hydrophilic acid–based pair regions became inter-connected with each other (Fig. 9), offering more conducting channels for the transportation of  $\text{H}^+$ . As a result, it achieved a high perm-selectivity of 333.3 between  $\text{H}^+$  and  $\text{Zn}^{2+}$  and extremely low  $\text{Zn}^{2+}$  leakage of 0.05%. Apparently, the improvement in membrane compactness via this approach blocked the  $\text{Zn}^{2+}$  transportation and increased the perm-selectivity of  $\text{H}^+$  significantly. Due to the phase-separation, the membrane area resistance was lower than that of the pristine SPPO membrane in acid solution, it was another advantage of this method [94]. It is suggested that the acid–base interaction can be considered as a promising way of preparing MCPMs by controlling the area resistance or perm-selectivity.

#### 5. Summary and Perspective

MCPMs especially possessing monovalent cation perm-selectivity have emerged as new type of IEMs which serve as the core components in traditional industries and innovative energy technologies. Since few decades, MCPMs have shown lots of potential applications such as production of sodium chloride [95], acid recovery in hydrometallurgy [61], removal of specific ions in liquid waste [18,96,97], lithium recovery from brine [8] and reverse electrodialysis for blue energy [5,98] benefiting from their high monovalent ion perm-selectivity compared to unmodified polymeric membranes. Although the current progress in exploring MPCMs is prominent, still there remain plenty of challenges, more detailed and systematic studies have to be made. For example, the limited current density should be promoted to ensure the high perm-selectivity in practical ED applications [24]. In addition, the "trade-off" effect between ionic flux and perm-selectivity is a big issue

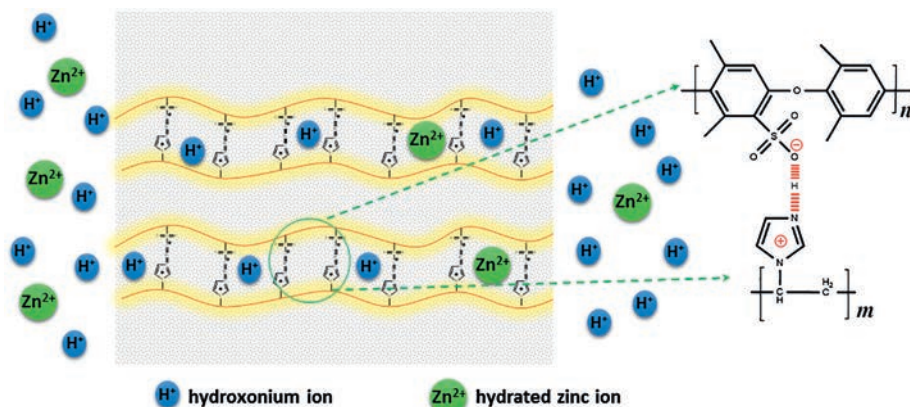


Fig. 8. Constructing  $\text{H}^+$  transfer channels in the membranes through the formation of acid–base pairs.



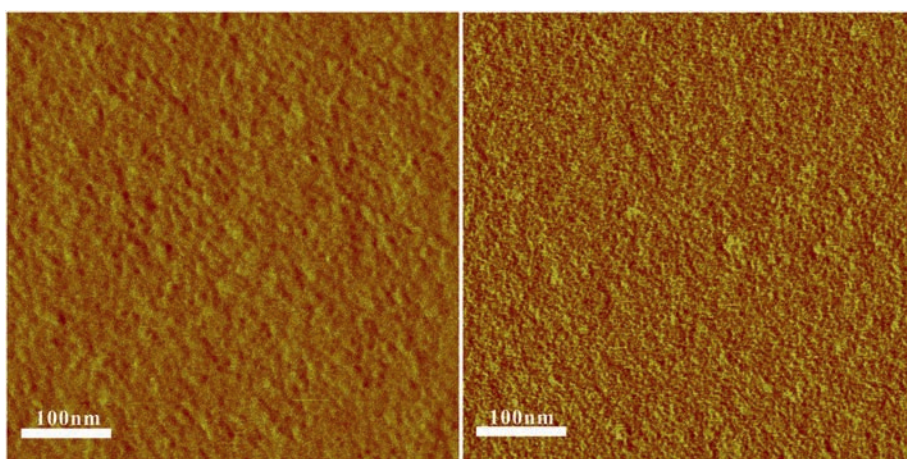


Fig. 9. AFM phase images of SPPO (left) and acid-base pair (right) membranes.

in fabrication of high-performance MCPMs as clearly presented in Fig. 10. It is clearly shown that the system of  $H^+$  and metallic ions is the easiest one to separate as compared to the other systems. Especially, the values of ionic flux and perm-selectivity of nanofiltration alike membrane for  $H^+/Zn^{2+}$  system lie in the attractive region, indicating the advantage of porous membrane for ion separation. Furthermore, constructing ion channels and introducing the auxiliary phase can be considered as promising ways of beating the “trade-off” effect. For  $K^+/Mg^{2+}$ ,  $Na^+/Mg^{2+}$  and  $Na^+/Ca^{2+}$  systems, which existed extensively in seawater, the ionic flux and perm-selectivity still remain unsatisfactory, either a low perm-selectivity with high ionic flux or a high perm-selectivity with low ionic flux. In a word, how to beat the “trade-off” effect and to get high-performance MCPMs with high perm-selectivity and ionic flux is a challenge that needs urgent solutions.

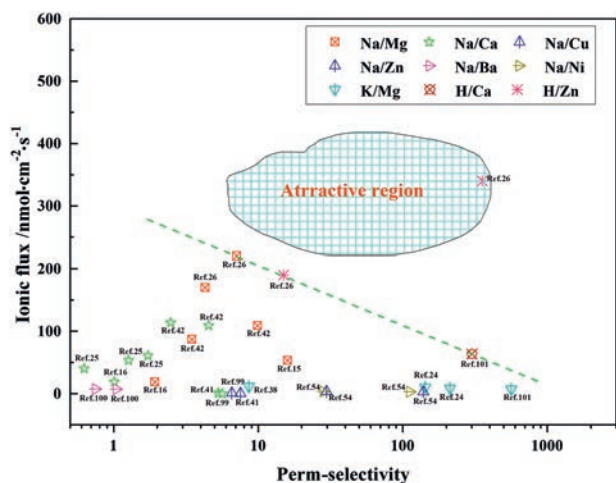


Fig. 10. Upper bound relationship for monovalent cation and multi-valent cation separation. Data collected from Refs. [15,16,24–26,38,41,42,54,99–101].

Generally, mono-/multi-valent cation separation depends on the pore-size sieving effect, the different Gibbs hydration energy of cations and the electrostatic repulsive forces, which are governed essentially by the affinity with the membrane and the relative migration speed in the membrane phase. Apart from the intrinsic characteristics of materials, choosing appropriate preparation methods is of pivotal importance to endow the perm-selective permeability to the traditional IEMs.

Currently, a series of approaches such as covalent cross-linking, surface modification, polymer blending, electrospinning, fabricating nanofiltration-like membrane, organic–inorganic hybrid and other technologies have been proposed, the prepared membranes show enhanced perm-selectivity by adjusting the affinity of the cations with membrane and their migration speed in the membrane phase. Each technique has their own advantages and limitation. For example, covalent cross-linking and annealing technologies can improve the compactness of the membranes and thus lead to an increase in perm-selectivity. However, it brings the high electrical resistance of the membranes. Surface modification technology is expected to obtain high ionic flux and low electrical resistance, but the long-term stability of modified layer or the complicated producing process still remains unsatisfactory. Simplicity is a big advantage for polymer blending and organic–inorganic hybrid technologies, nevertheless, a significantly improved perm-selectivity is unable to be achieved due to the limitation on the inherent properties of the used components. Some emerging technologies, such as electrospinning, constructing ion channels and introducing porous structure in the membranes, could prepare MCPMs with preferable properties. Further researches should be considered to investigate the mechanisms of the perm-selective process in MCPMs and how the specific parameters affect the performances.

In addition, available ion separation mechanisms should be proposed by means of deep understanding towards the ion transport issues within a confined space of ionic channels [102]. MCPMs in the use of functional porous materials such as polymers of intrinsic micro-porosity (PIM), Tröger's Base (TB), metal–organic frameworks (MOFs) and covalent organic frameworks (COFs), are also gradually applied for ionic separation due to the controllable framework structure and pore size as well as ion exchange/adsorption ability. Furthermore, layered-dimensional materials with unique atomic thickness and micrometer lateral dimensions, such as zeolite [103], graphene oxide [21,104] and 2D  $MoS_2$  nanosheets [105] have been explored increasingly as fundamental platforms to develop ion transport and separation technologies [106]. Finally, these new materials and manufacturing methods would endow the membranes with excellent monovalent cation perm-selectivity, considerable monovalent cation flux, low electrical resistance, high limited current density and long-term stability.

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