



Review

Removing halide ions from sulfate solutions by anion exchange membranes in electro dialysis process: Recent advances, challenges, and prospects

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ARTICLE INFO

Editor: Gaohong He

Keywords:

Halide ions
Sulfate ions
Anion exchange membranes
Ion selectivity
Electrodialysis
Ionic characteristics

ABSTRACT

Removing halide ions from wastewater and industrial effluents is crucial to eliminating their potential risks to human health, ecosystems, and industrial operations. However, conventional techniques for this process are inefficient and have severe drawbacks, including the use of hazardous chemicals, secondary pollution, and increased costs. Utilizing monovalent selective anion exchange membranes (AEMs) in electro dialysis has emerged as an effective solution for separating halide ions from sulfate-rich solutions. This review presents the recent progress, applications, and future prospects of this method, elucidates the principles underlying monovalent selectivity in AEMs, provides an overview of AEM membrane materials and preparation methods, and addresses the impacts of electro dialysis operating conditions on halide removing processes, such as current density, flow rate, pH, and stack design. Existing challenges and recognized gaps, such as complexities in solution composition, membrane stability concerns, insufficient consideration of operational factors, and limitations in modeling, demanding further efforts in this field are also presented. Overcoming these hurdles necessitates a focused approach involving material and membrane design, in-depth exploration of solution dynamics, better operational understanding, and the application of advanced modeling techniques. Effectively addressing these challenges holds the potential to notably amplify the efficiency and efficacy of electro dialysis in mitigating halide ion pollution in sulfate-rich solutions.

1. Introduction

In recent years, growing concerns have arisen regarding the presence of halide ions in sulfate-rich solutions within both modern industrial processes and natural water bodies. The sources of halide ions can range from natural aquatic environments to product streams generated by chemical manufacturing processes and operations such as metal smelting, flue gas desulfurization, and seawater desalination [1,2]. The presence of these ions negatively impacts not only industrial equipment and operations but also aquatic life, soil quality, and overall water resources upon discharge into natural water bodies [3–5]. Hence, addressing halide ion contamination in sulfate-based water sources and

industrial effluents is essential to prevent environmental pollution, safeguard ecosystems, and preserve equipment.

The quantity of halide ions present in the solution can vary for each origin, depending on both natural factors and industrial activities. For instance, the naturally occurring high levels of fluoride and chloride in groundwater continue to be a worldwide health concern, as they are detrimental not only to human health but also the broader ecosystem. The World Health Organization maintains a guideline of 1.5 mg·L⁻¹ for fluoride and 150–250 mg·L⁻¹ for chloride in drinking water [6–8]. Nevertheless, based on a global predictive model that employs machine learning techniques, the projected total population at risk of encountering fluoride concentrations surpassing 1.5 mg·L⁻¹ falls within the

Abbreviations: IEM, ion exchange membrane; AEM, anion exchange membrane; CEM, cation exchange membrane; PAEK, poly(arylene ether ketone); PAES, poly(arylene ether sulfone); BPPO, poly(2,6-dimethyl-1,4-phenylene oxide); IEC, ion exchange capacity; CMPSF, chloromethylated polysulfone; PAN-co-PnBA-co-PDMA, poly(acrylonitrile-co-n-butyl acrylate-co-dimethylamino ethyl methacrylate); PAN-co-PVIm, polyacrylonitrile-co-poly(vinylimidazole); DAS, 4,4-diazo-stilbene-2,2-disulfonic acid disodium salt; sPSF, sulfonated polysulfone; KANF, kevlar amide nanofibers; HACC, hydroxypropyltrimethyl ammonium chloride chitosan; LbL, layer-by-layer; PSS, poly(sodium 4-styrene sulfonate); PAH, poly(allylamine hydrochloride); MGOFs, multilayer graphene-organic frameworks; SDDS, sulfonated 4,4'-diaminodiphenyl sulfone; QCS, quaternized chitosan; NSBC, N-O-sulfonic acid benzyl chitosan; L-Dopa, L-3,4-dihydroxyphenylalanine.

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<https://doi.org/10.1016/j.seppur.2023.125767>

Received 21 September 2023; Received in revised form 4 November 2023; Accepted 16 November 2023

Available online 19 November 2023

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range of 63–330 million individuals (Fig. 1). This underscores the urgent need to concentrate efforts on reducing fluoride exposure [9].

Another situation where the presence of halide ions poses challenges is within the metal production industry. A case in point is the domain of zinc smelting, where chloride and fluoride ions are typically found at concentrations ranging from 20 to 320 mg·L⁻¹ and 100–200 mg·L⁻¹, respectively, and sulfate ions are present at much higher levels, around 250–300 g·L⁻¹ [10,11]. As halide ions enter the leachate and continue to circulate within the electrolytic system, the electrode plates experience constant corrosion, eventually leading to the halt of the electrolysis process [12]. Hence, in the production of electrolytic zinc, it becomes crucial to ensure that their concentration remains within the range of 50–100 mg·L⁻¹. Numerous examples of industrial processes suffering from the presence of halide ions at different compositions in sulfate-based solutions can be exemplified [13,14], requiring urgent attention for their selective removal.

To tackle these challenges, there is a growing urgency to develop and implement effective halide ion removal technologies across various industrial applications. By adopting sophisticated treatment approaches like ion exchange, adsorption, membrane filtration, and chemical precipitation, industrial facilities can successfully remove halide ions from sulfate-rich wastewater [13,14]. However, these techniques were reported to have significant drawbacks, such as using highly hazardous chemicals, generating large amounts of sludge requiring safe disposal, and taking high operating costs and long reaction times [15]. These shortcomings emphasize the critical need for innovative and environmentally friendly approaches to this issue.

Among the various methods explored, the technology based on ion exchange membranes (IEMs) stands out as an attractive method for treating industrial effluents [16–18]. In particular, monovalent selective anion exchange membranes (AEMs) have emerged as a promising solution for effectively reducing halide ions content in sulfate solutions in electro dialysis [19,20]. These semipermeable barriers possess selective ion transport characteristics, enabling efficient separation of halide ions from sulfate solutions. On top of that, electro dialysis has the capacity to treat a substantial volume of effluents containing dilute concentrations of targeted ions in a short period [21]. This efficiency is complemented by its lower energy consumption and potential for regeneration, which contribute to improved energy efficiency and reduced waste generation. As a result, AEMs in electro dialysis can offer a promising and environmentally friendly solution for sustainable industrial wastewater treatment, causing less environmental impact compared to conventional technologies.

Several review articles have examined the subject of anion separation in the literature. In 2000, Sata et al. [22] conducted a review that primarily focused on the impact of hydrophilicity of AEMs on selective anion separation. In 2017, Khoiruddin et al. [23] outlined various

approaches centered around surface modification of IEMs, discussing their performance in energy conversion and ion selectivity. In 2018, a comprehensive review by Luo et al. [24] covered IEMs, including the separation of both anions and cations, advancements in fabrication techniques, mechanisms of ion transport, and experimental approaches for determining ion selectivity. In 2020, Besha et al. [25] highlighted recent progress in studying the effects of multivalent ions on power generation through reverse electro dialysis, in which the strategies for developing monovalent ion selective membranes received limited coverage. In 2021 and 2022, Pillai et al. [13] and Li et al. [14] reviewed fluoride and chloride elimination methods from water sources, primarily focusing on conventional technologies, with membrane processes being only briefly mentioned.

This review presents advancements in membrane materials, process optimization, including the development of AEMs, and the impact of operating conditions on the removal of halide ions from sulfate solutions. A concise overview of the relevant theory and background is provided as the basis for discussion, covering the concept of ion selectivity, characteristics of ions that govern their permeation through AEMs, and critical separation parameters. The principles underlying the removal of halide ions through AEMs in electro dialysis are extensively discussed, emphasizing the fundamental factors that influence the monovalent selectivity and transport mechanisms of halide ions. Additionally, the applications of AEM-based technology across diverse industries with real industrial solutions, where efficient halide ions removal is crucial, are summarized. The challenges and gaps in AEM-based halide ion removal techniques are highlighted. By illuminating recent advancements and potential future outlooks within this field, this review aims to enhance comprehension regarding sustainable approaches for addressing halide ion pollution.

2. Theory and background

2.1. Electro dialysis: Working principle and set-up

Electro dialysis is an electrochemical separation process that employs an electric field to selectively move ions through IEMs [26,27]. This technique is utilized for the separation and concentration of ionic species from solutions. Fig. 2 illustrates an electro dialysis configuration with two distinct types of IEMs placed alternately between electrodes: cation exchange membranes (CEMs) and AEMs. CEMs permit positively charged ions (cations) to transfer, whereas AEMs permit negatively charged ions (anions) to pass through. Electrodes are positioned at both ends of the membrane stack and are connected to an external power source that generates an electric field across the membranes. The membrane stack is divided into alternating compartments containing the solution to be treated, separated by the IEMs. As ions move across

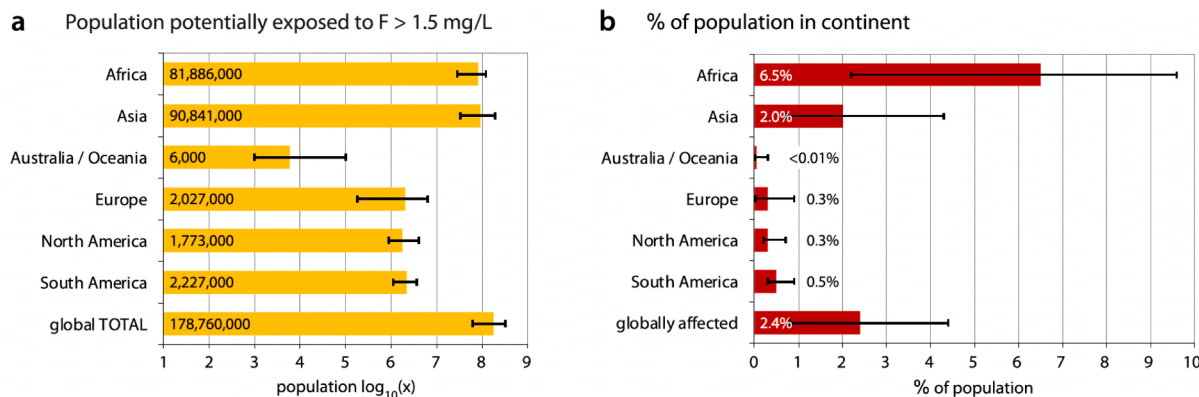


Fig. 1. Illustration depicting the population that might be subjected to fluoride concentrations exceeding 1.5 mg·L⁻¹ in groundwater: (a) the count of individuals potentially impacted by continent; and (b) the proportion relative to the overall population [9].

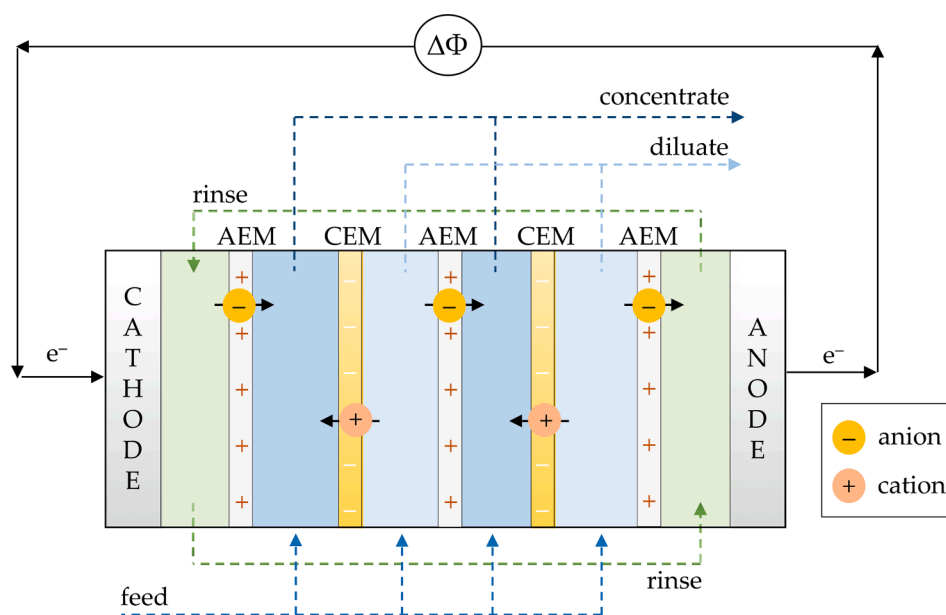


Fig. 2. Illustration depicting an electrodiolysis stack [26].

the membranes, they accumulate in the concentrate compartment, while being desalinated in the diluate compartment.

2.2. AEMs

AEMs are polymer films incorporating fixed, positively charged functional groups within their polymer matrix [28]. The microstructure of AEMs plays a pivotal role in determining their properties and performance, as depicted in Fig. 3. The polymer matrix of an AEM can consist of a range of materials, including fluorinated polymers, aromatic polymers, or other synthetics with ion-conductive capabilities [29]. These polymer chains become entangled, forming a network structure. The key functional groups responsible for anion exchange are mostly quaternary ammonium groups attached to the polymer backbone [30]. The density and arrangement of these functional groups profoundly impact the ion transport characteristics of the membrane [22]. The configuration of functional groups and polymer chains can establish ion-conductive pathways or channels within the membrane, facilitating the movement of anions while constraining the mobility of cations. These characteristics render AEMs the crucial components in electrochemical devices where the separation and control of different ions are of

paramount importance.

The internal structure of an AEM can be conceptualized as comprising three segments [31]:

- (i) The gel phase within an AEM refers to the region where water and ions are absorbed, forming a hydrated network. The gel phase is enriched with ionizable functional groups, often quaternary ammonium or other types of cationic groups. These groups are responsible for facilitating the ion exchange process by allowing anions to move through the membrane in the surrounding solution.
- (ii) An interstitial phase is located within the membrane's core, consisting of pores, voids, or defects containing an electrically neutral solution between gel regions. This phase predominantly functions as a non-selective pathway facilitating the passage of all water-soluble substances.
- (iii) The hydrophobic domain in an AEM refers to regions within the polymer structure that lack fixed ionic groups. This phase acts as a physical barrier, preventing the uncontrolled passage of molecules and reducing the risk of membrane swelling and the subsequent loss of mechanical integrity.

2.3. Ionic characteristics

The transport of ions through an IEM is influenced by both thermodynamic factors (membrane's affinity for the ion) and kinetic factors (mobility through the membrane) [32]. These considerations are affected by the distinct physicochemical characteristics of ions, including their ionic radius, charge density, hydrated radius, and hydration free energy. Understanding these characteristics is crucial for maintaining desired selectivity.

The ionic radius refers to the size of an ion, which is the distance between the nucleus and the outermost electron of the ion [33]. The hydrated size of an ion takes into account the size of the ion along with the water molecules that surround it in a solution [34]. Ion transport in a solution is associated with the size of hydrated ions rather than ionic radius because, when ions dissolve in water, they attract water molecules, which arrange themselves around the ions in a process called hydration [35]. The degree of hydration is directly influenced by the charge density of an ion, referring to the ratio of the charge of the ion to its effective volume [36–38]. Ions with smaller ionic radius possess

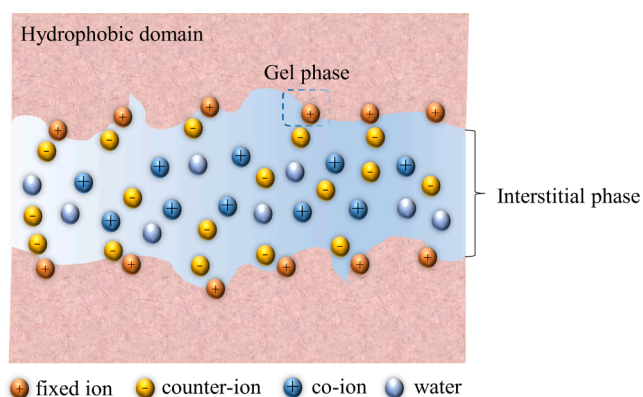


Fig. 3. Illustration depicting an AEM structure. The gel phase refers to a state in which the polymer matrix holds onto fixed ionic groups and enables the movement of counter-ions. The interstitial phase involves the movement of co-ions. The hydrophobic domain does not contain any fixed ionic groups [31].

higher charge densities and typically attract a greater number of water molecules (Fig. 4). As one moves down the halogen group in the periodic table, the ionic size generally increases, while the hydrated size of halide ions decreases due to variations in charge density, indicating an inverse relationship between ionic radius and hydrated radius (Table 1).

Ion transport through membranes might also involve a fractional loss of the water from the hydration shell of ions as they enter the membrane. This phenomenon is connected to the hydration free energy of ions. The energy necessary to shed water molecules originates from the attractive interactions between ions and oppositely charged groups bound within the membrane [41,42]. The extent of dehydration is determined by the hydration energy of the ions. A lower free energy of hydration makes it easier for the ions to release water molecules from their hydration shells [43].

The transport order of ions is significantly influenced by the above-mentioned ionic properties. Based on the findings from transport tests conducted through both aqueous gel sieving chromatography and AEM, it was observed that small monovalent ions (like fluoride) exhibit stronger attachments to water molecules compared to larger monovalent ions (such as chloride and bromide) as they transport through the gel matrix [44,45]. This suggests that larger monovalent ions undergo partial dehydration and adhere to the nonpolar gel surface. This phenomenon can be attributed to ions with larger radii forming weaker associations with water molecules due to their smaller charge densities than small monovalent ions. This understanding aligns with the order of adsorption for anions onto the AEMs: bromide > chloride > fluoride. This order of adsorption inversely corresponds to their hydration energy. When sulfate ions are present within the mixture, the generalized transport order becomes (bromide > chloride > sulfate > fluoride) [24]. Given that both sulfate and fluoride ions have high hydration energies, sulfate ions are preferentially exchangeable into the AEMs due to their higher valency. This preference underscores the intricate interplay of ion size, charge density, and hydration energy in their interactions with membranes and water molecules.

2.4. Ion selectivity and separation parameters

The selectivity between two counter-ions [P_B^A] is often defined to be the relative rate of permeance of the desired (or target, A) counter-ions to the additional feed counter-ions (B). $P_B^A > 1$ indicates a favorable transport of component A with respect to component B. Ion selectivity between two counter-ions can be calculated as follows [46]:

$$P_B^A = \frac{t_A C_B}{t_B C_A} \quad (1)$$

where t_A and t_B are the transport numbers of the components A and B, while C_A and C_B ($\text{mol}\cdot\text{L}^{-1}$) are the concentrations at the membrane surface of the desalting side of the system.

Selectivity among the coexistence of competitive counter-ions in a process like electrodialysis involves the preferential transport of certain ions over others through ion-selective membranes, even when multiple

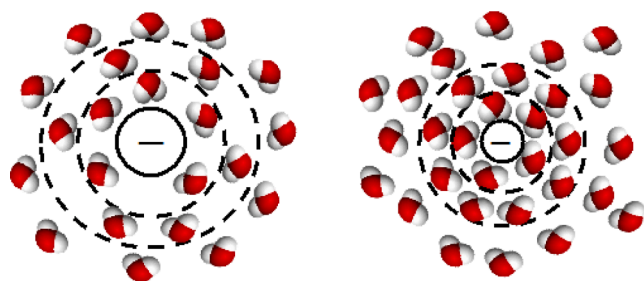


Fig. 4. Illustration depicting hydration shells around a large and a small anion. The figure is adapted with permission from [34] (Copyright © 2006, Elsevier).

Table 1
Ionic characteristic of anions.

| Anion | Ionic radius (Å) [39] | Hydrated radius (Å) [39] | Charge density ($\text{C}\cdot\text{mm}^{-3}$) [38] | Hydration free energy ($\text{kJ}\cdot\text{mol}^{-1}$) [40] |
|-------------|-----------------------|--------------------------|---|--|
| F^- | 1.17 | 3.52 | 24 | -465 |
| Cl^- | 1.67 | 3.32 | 8 | -340 |
| Br^- | 1.82 | 3.30 | 6 | -315 |
| SO_4^{2-} | 2.44 | 3.79 | 5 | -1145 |

ions are present and in competition for passage. In scenarios involving the coexistence of two or more competitive counter-ions, such as halide ions and sulfate ions, a range of parameters dictating ion selectivity has been found to play a significant role (Fig. 5). The selectivity of IEMs is subject to the influence of electrostatic barriers and dielectric effects, both of which are rooted in the differences in ion valency, size, and hydration energies, in conjunction with the distinctive properties of the membrane material [32,47]. Differences in the electrostatic interaction between counter-ions and the membrane surface give rise to an electrostatic barrier effect, as depicted in Fig. 5a. To elaborate, the membrane surface, whether it possesses an opposite charge or an identical charge to that of the counter-ion, demonstrates a heightened electrostatic interaction for counter-ions with greater valency or larger size within the same valency. This electrostatic preference influences the transport of specific counter-ions through the membrane, potentially leading to their selective movement based on these electrostatic attributes. Dielectric effects, influenced by the energy of hydration of an ion, along with the hydrophobicity of the membrane, is another parameter that affect ion selectivity. In this scenario, the selectivity is governed by the process in which the ion partially releases its water molecules, with ions possessing lower hydration energy shedding water molecules more readily (Fig. 5b). This facilitates the passage of ions through the hydrophobic membrane. Moreover, steric hindrance emerges as another pivotal determinant governing the preferential selection of counter-ions by limiting the partitioning of larger ions within densely structured IEMs (Fig. 5c). [42]. This differentiation in ion ingress rates arises from the hydrophilic entrance dimensions into the IEM, typically falling within the sub-nanometer scale, where smaller ions penetrate faster in comparison to larger ions.

The ability to distinctively separate counter-ions is also impacted by the operational conditions of electrodialysis (i.e., current density and flow rate) [48–50]. At the solution-membrane interfaces, towards the dilute and concentrate compartments, boundary layers emerge when an electric potential is imposed on the cell, in which the ion transport rates are controlled by diffusion. These boundary layers are a result of the enhanced transport rate of counter-ions in the membrane compared to the solution, leading to the depletion of ions at the membrane-solution interface towards the dilute compartment and ion accumulation towards the concentrate compartment [28]. The management of these operational factors is crucial for achieving specific ion selectivity because ions diffuse across the boundary layer at distinct rates. Most importantly, the current density controls which of the several transport mechanisms arising from membrane-ion interactions and diffusive transport of ions across the boundary layers has the most dominant impact on competitive ion transport. The boundary layer effect is exploited most effectively when the competing ions differ in their concentration. For instance, in Fig. 5d, the applied current exceeds the limiting current for anion 2, meaning that the transport of anion 2 has reached its maximum and is limited by its diffusion rate through the boundary layer. Conversely, anion 1 has not reached its maximum transport rate, and a further increase in electric current will lead to an enhanced transport rate of this ion. Evidently, the ratio between the operating current and ion-specific limiting currents of the competing species can alter the relative transport rates between competing counter-

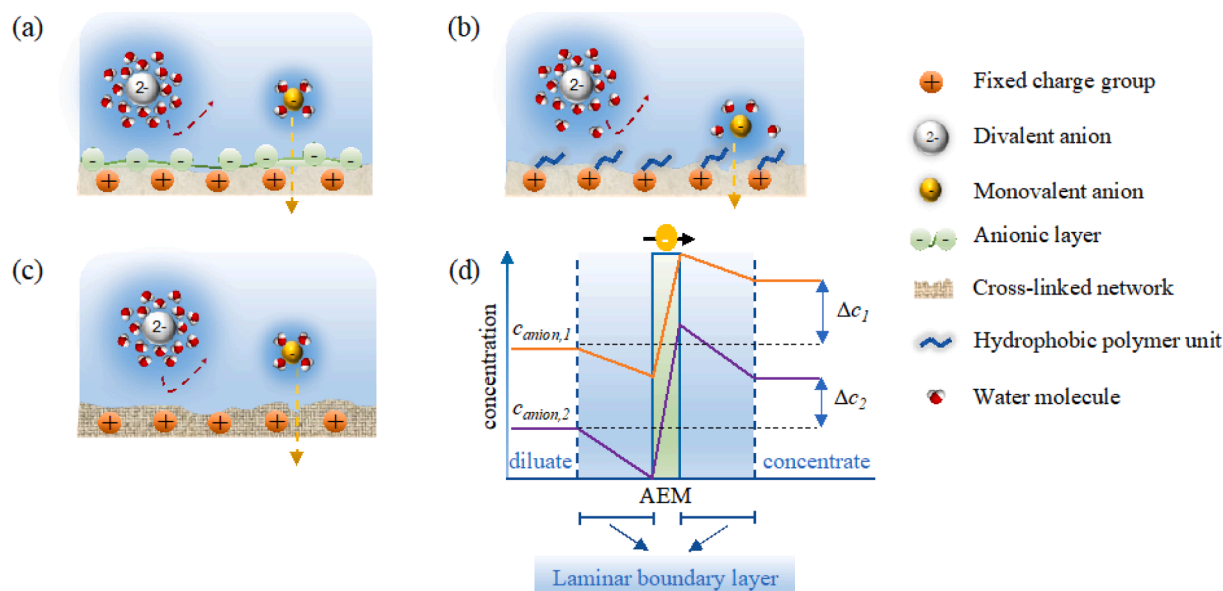


Fig. 5. Distinct factors affecting ion selectivity: (a) electrostatic barrier effect: a negatively charged layer on AEM repels higher valency anions more than monovalent ones; (b) dielectric effect: increasing membrane hydrophobicity hinders passage of highly hydrated anions more than less hydrated ones; (c) sieving: cross-linking creates a tight network, limiting the passage of larger anions while allowing smaller ones; and (d) boundary layer separation: ion depletion in the boundary layer facing the diluate compartment separates competing counter-ions based on concentration, ion characteristics, and the applied current [26].

ions [51,52].

3. Progress in AEMs for halide ions removal using electro dialysis

The recent advances in AEMs for halide ions removal from sulfate solutions using electro dialysis involve various aspects, including the research and development progress in AEM preparation methods and the control of operating conditions.

3.1. AEM preparation methods

3.1.1. Microstructurally designed AEMs

Tuning the structure of the AEM matrix proves to be an effective method for enhancing ion selectivity. This can be achieved by incorporating functional groups into the polymer matrix or embedding inorganic components, which can alter its hydrophilic character, channel size, charge density, and swelling characteristics. These parameters significantly influence the selectivity between ions.

3.1.1.1. Chemically-grafted network. Adjusting the membrane microstructure holds significant relevance for counter-ion fractionation. Previously, the importance of hydration free energy has been emphasized as a crucial characteristic for ion permeation order through the membrane. In particular, the hydrophobic domains can impede the permeation of strongly hydrated ions, while less hydrated ions can easily pass through the membrane. The manipulation of hydrophobicity in the membrane can be achieved by introducing alkyl side chains of varying lengths. A side-chain-type AEM offers prominent hydrophilic/hydrophobic discrimination, as the flexible functionalized segments and unfunctionalized backbones yield a micro-phase separated structure. This microstructure is beneficial for promoting high mobility of counter-ions on conductive groups within the membrane.

The common strategy to create monovalent selective AEMs includes hindering the the passage of strongly hydrated anions while favoring the permeation of less hydrated ones through the membrane. This strategy involves the utilization of a series of fluoro-methyl poly(arylene ether)s functionalized with long-side-chain imidazolium salts. Liao et al. [53] synthesized fluoro-methyl poly(arylene ether ketone) (PAEK) polymers through nucleophilic substitution polycondensation, followed by

grafting with varying amounts of long-side-chain imidazolium groups with hexyleneoxy spacers. AEMs with higher quantities of long-side chains exhibited a monovalent anion selectivity of 7.70 after 30 min of electro dialysis operation. The selectivity was attributed to the presence of hydrophilic, conductive, and flexible side-chain imidazolium groups combined with a rigid hydrophobic backbone in the AEM matrix, enabling micro-phase separation at the nano-scale. Later, they fabricated four side-chain-type imidazolium salt-tethered poly(arylene ether sulfone) (PAES-NH₂) AEMs with different alkyl spacer lengths (3, 6, 9, and 12) (Fig. 6) [54]. The AEM with a hexyl alkyl spacer modification demonstrated a superior selectivity of 7.10 compared to the other three variants (3.48, 6.81, and 4.26). This was attributed to the fact that a longer hydrophobic alkyl spacer decreased the hydrophilicity of the side chains, resulting in a reduced degree of phase separation, thereby leading to lower selectivity.

Researchers have reported various side-chain-type homogeneous AEMs designed for different polymer backbones to facilitate the separation of chloride and sulfate anions. For instance, Irfan et al. [55] synthesized three variants of AEMs based on quaternization of brominated poly(2,6-dimethyl-1,4-phenyl oxide) (BPPO), each with varying alkyl spacer lengths (Fig. 7). The AEM with the longest alkyl spacer exhibited a selectivity of 13.07 between chloride and sulfate ions. The inclusion of the undecyl side chain (with an alkyl spacer length of 11) led to a more pronounced micro-phase separation between hydrophilic and hydrophobic domains. This configuration enhanced chloride ion transport by creating a favorable hydrophobic environment. However, the permeation of sulfate ions was impeded due to increased hydrophobicity resulting from longer alkyl side chains. Wang et al. [56] also developed BPPO-based AEMs functionalized with long-chain tertiary amines of varying alkyl chain lengths up to 16 for electro dialysis of chloride/sulfate solutions. A direct correlation was observed between the alkyl chain length of tertiary amines and the resulting selectivity values. The maximum selectivity achieved was 12.84 achieved with the membrane incorporating the longest alkyl chain length, suggesting better monovalent selectivity performance compared to commercial ASV AEM (6.52). Moreover, heat treatment helped achieve monovalent ion selectivity through a pore-size sieving effect due to modulating membrane compactness. However, this improvement in selectivity came at the expense of a high membrane resistance (101 Ω·cm²). A higher molar

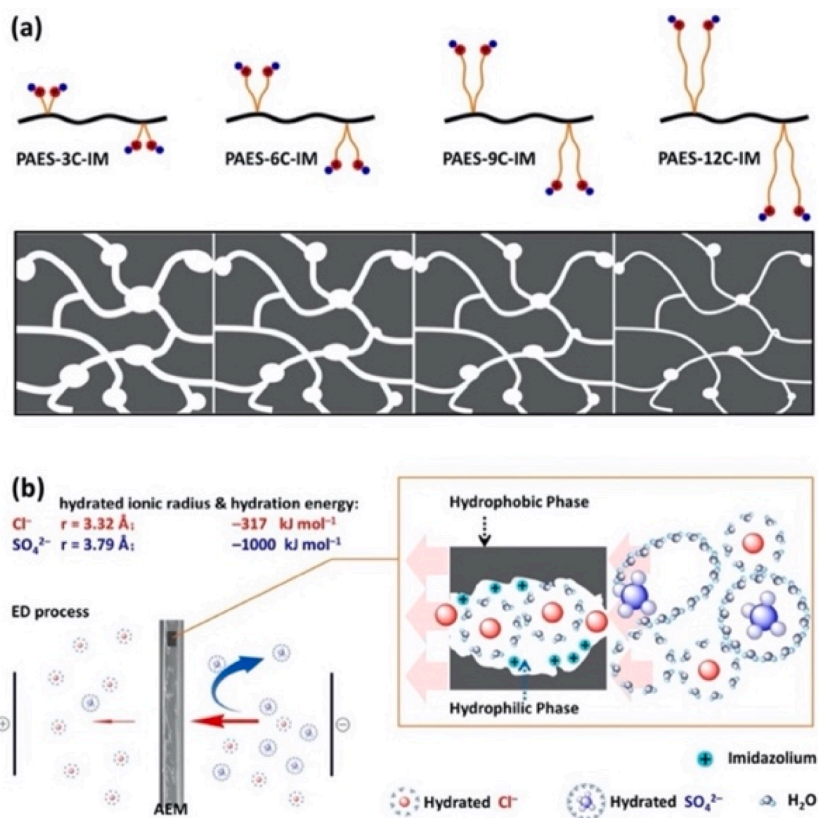


Fig. 6. Illustration depicting (a) AEMs with different alkyl spacers and (b) ion selectivity mechanisms. The figure is reprinted with permission from [54] (Copyright © 2020, Elsevier).

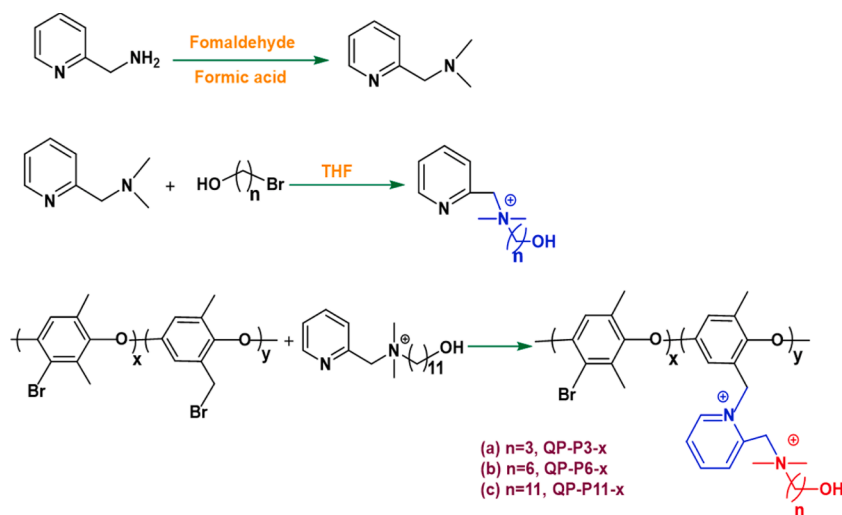


Fig. 7. Illustration depicting the route for the synthesis of monovalent selective AEMs with different alkyl spacers. The figure is reprinted with permission from [55] (Copyright © 2019, American Chemical Society).

ratio of tertiary amine to bromobenzyl in BPPO reduced selectivity but increased water uptake and ion exchange capacity (IEC), favoring sulfate ion transport over chloride ions.

Wang et al. [57] synthesized long-side-chain-type AEMs by altering the polymer backbone to quaternized chloromethylated polysulfone (CMPSF) (Fig. 8), aiming to investigate the selectivity of chloride and sulfate ions. AEMs with the longest alkyl chain ($n = 16$) achieved an excellent selectivity of 60.1 by adjusting hydrophilic/hydrophobic phase separation. However, they had low IEC and high hydrophobicity, resulting in a relatively high area resistance of $95.2 \Omega\text{-cm}^2$, making

electrodialysis energy-demanding. AEMs with two cations along long alkyl side chains ($n = 16$) showed lower selectivity (<5) due to increased charge densities, reducing hydrophobicity. These findings shed light on the importance of balancing AEM composition and structure for optimizing ion selectivity and membrane performance. Very recently, Goel et al. [58] also employed CMPSF in their work, synthesizing a range of monovalent anion selective membranes through cross-linking CMPSF with 1,4-diazabicyclooctane functionalized graphene oxide. The cross-linking with the polymer matrix led to an enhancement in selectivity for chloride/sulfate, increasing it from 1.7 for the pristine membrane to

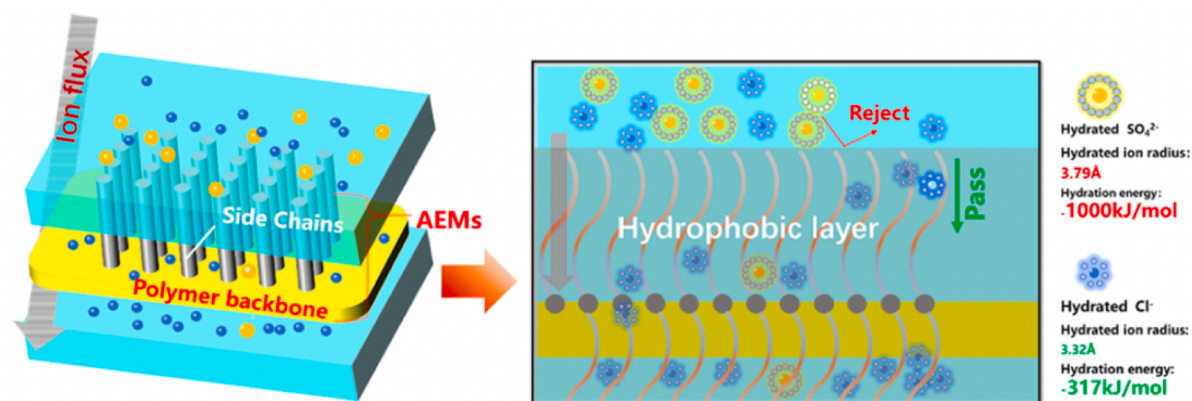


Fig. 8. Illustration depicting ion selectivity mechanisms for the prepared AEMs grafted with long alkyl chains. The figure is reprinted with permission from [57] (Copyright © 2021, American Chemical Society).

5.7.

The cross-linking strategy was also employed in subsequent investigations aimed at synthesizing different membrane microstructures. Pal et al. [59] conducted a study focusing on the synthesis of cross-linked terpolymer-based AEMs featuring modifiable polarity around the cationic centers. This was achieved through the cross-linking of a quaternized terpolymer, specifically poly(acrylonitrile-co-n-butyl acrylate-co-dimethylamino ethyl methacrylate) (PAN-co-PnBA-co-PDMA), using hydrazine hydrate. The primary objective of the study was to facilitate the efficient separation of chloride from sulfate through the utilization of electro dialysis processes. The resulting membrane exhibited a selectivity of 4.76, which was attributed to the length of the alkyl chain and the inherent hydrophobic characteristics of the micro-environment encompassing the quaternized nitrogen centers. Subsequently, Mondal et al. [60] conducted a study focused on the preparation of a series of cross-linked AEMs with imidazole rings derived from the copolymer polyacrylonitrile-co-poly(vinylimidazole) (PAN-co-PVIm). The synthesis involved N-alkylation with alkyl halides of distinct chain lengths (carbon numbers: 1, 6, 10, 18) followed by a reaction with 1,6-diaminohexane. By introducing alkyl chains of greater length (18 carbon number), the hydrophobicity of the membrane was effectively tuned, resulting in a notable selectivity of 14.5 between chloride and sulfate ions. The heightened selectivity is due to the rigid imidazolium structure and locally organized longer alkyl chains, which create steric hindrance, impeding the passage of hydrophilic sulfate anions (Fig. 9).

The zwitterion structure of modified membranes also allows for the tuning of ion selectivity. In a study by Liao et al. [61], amphoteric AEMs were synthesized by incorporating long-side-chain imidazolium-functionalized PAES cross-linked with 4,4-diazo-stilbene-2,2-disulfonic acid disodium salt (DAS) for electro dialysis applications. The hydrophilic

phase contained imidazolium/sulfonated groups, while the hydrophobic phase consisted of the aromatic polymer backbones and aliphatic chains from pendants/cross-linkers. The resulting membranes exhibited a selectivity of 12.5 for chloride/sulfate during a 1-hour electro dialysis process. In their subsequent study, three amphoteric AEMs were prepared by blending amino-containing PAES with 10, 15, and 20 wt% of sulfonated polysulfone (sPSF), followed by grafting imidazolium salt-terminated side alkyl chains onto the PAES backbone [62]. The modified membrane with 15 wt% of sPSF displayed a selectivity of 21.8 between chloride and sulfate during the electro dialysis process. These favorable results were attributed to the synergistic effects of (i) electrostatic repulsion difference from the negatively charged sulfonate groups against monovalent chloride ions and divalent sulfate ions, (ii) hydration free energy difference between ions, and (iii) the pore-size sieving effect of the dense matrix structure resulting from cross-linking (Fig. 10).

The findings above elucidate the critical role of alkyl side chain length and hydrophobicity in influencing ion selectivity within the investigated AEMs, providing valuable insights for the rational design and optimization of AEM materials for selective chloride/sulfate separation. However, when the selectivity of fluoride from sulfate is of interest, hydrophobic membranes are no longer suitable. This is due to the strong water-binding capability of fluoride, which restricts its transport ability through the hydrophobic structure. Considering the difficulty of the desired separation between fluoride and sulfate, novel strategies have been proposed. In a recent study by Zhao et al. [63], they developed a novel AEM utilizing Kevlar amide nanofibers (KANF) to facilitate efficient fluoride capture. The incorporation of positively charged groups into the KANF's framework was achieved through the self-assembly of hydroxypropyltrimethyl ammonium chloride chitosan (HACC), involving the formation of amide bonds. Additionally, the

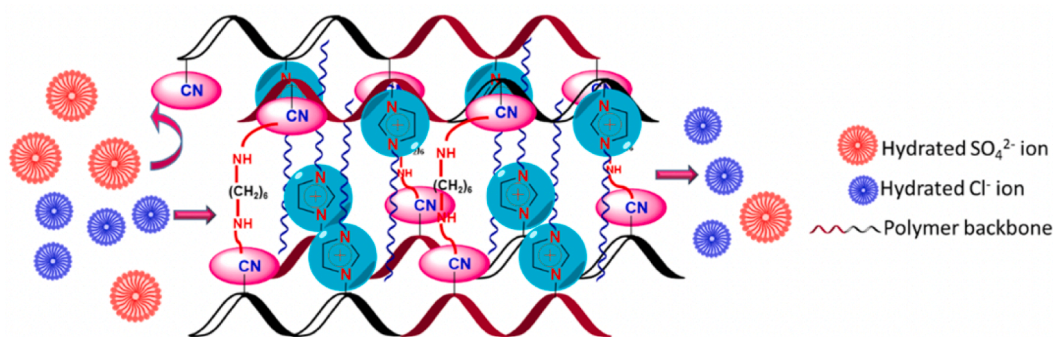


Fig. 9. Illustration depicting the chloride and sulfate transport through AEM. The figure is reprinted with permission from [60] (Copyright © 2023, American Chemical Society).

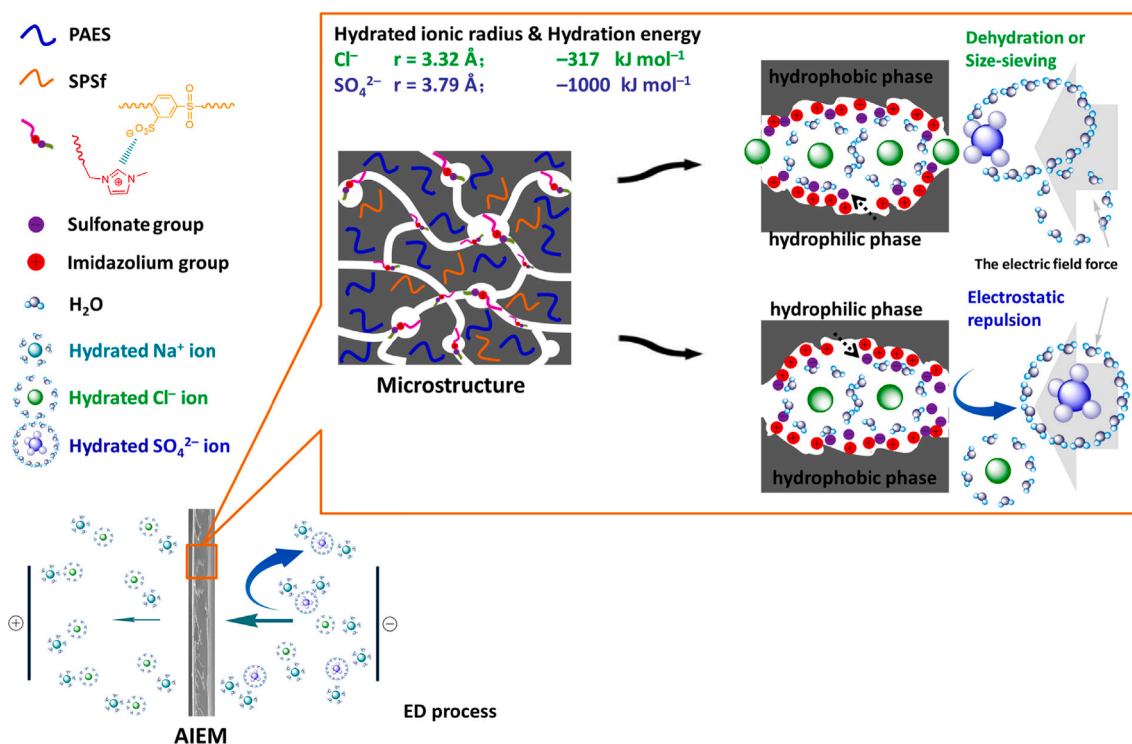


Fig. 10. Illustration depicting ion selectivity mechanism for the prepared AEMs. The figure is reprinted with permission from [62] (Copyright © 2020, Elsevier).

membrane surface underwent sulfonation to enhance fluoride selectivity. The resultant membrane exhibited a selectivity of 2.75 for fluoride/sulfate ions, demonstrating promising potential for effective fluoride ion separation from sulfate.

Very recently, Tekinalp et al. [20] developed monovalent selective AEMs tailored for the simultaneous separation of fluoride and chloride from sulfate in electrodialysis. They synthesized a series of BPPO polymers with controlled bromination degrees at both benzyl and aryl positions. These polymers were subsequently quaternized using various tertiary amines with differing chain lengths to engineer optimized AEMs. To enhance their monovalent selectivity, selected AEMs underwent surface modification through layer-by-layer (LbL) deposition of poly(sodium 4-styrene sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) polyelectrolytes (Fig. 11). Consequently, the resulting AEMs exhibited significantly improved selectivity values of 11.7 for chloride/sulfate and 8.3 for fluoride/sulfate, surpassing the selectivity of a commercial monovalent selective ASVN membrane. This performance was attributed to the precise adjustment of the membrane

microstructure, maintaining a moderate level of hydrophobicity and a compact structure, which was combined with a sufficiently high charge density, facilitating an ample capacity for polyelectrolyte adsorption. Simultaneously optimizing both membrane microstructure and surface can prove to be an effective strategy for the separation of closely related counter-ions in an electrodialysis process.

The hydrophobicity of the membrane can be manipulated through the incorporation of distinct long alkyl side chains. This manipulation undeniably exerts a pronounced influence over the membrane’s physicochemical and electrochemical characteristics, thus leading to a decisive impact on ion selectivity. The comprehensive investigation of these hydrophobicity-driven effects on the microstructure and performance of the developed AEMs is summarized in Table 2.

3.1.1.2. Hybrid membranes. In recent years, there has been considerable interest in hybrid IEMs that incorporate both polymeric substances and inorganic components. This is primarily because these hybrid membranes combine the benefits of organic and inorganic materials.

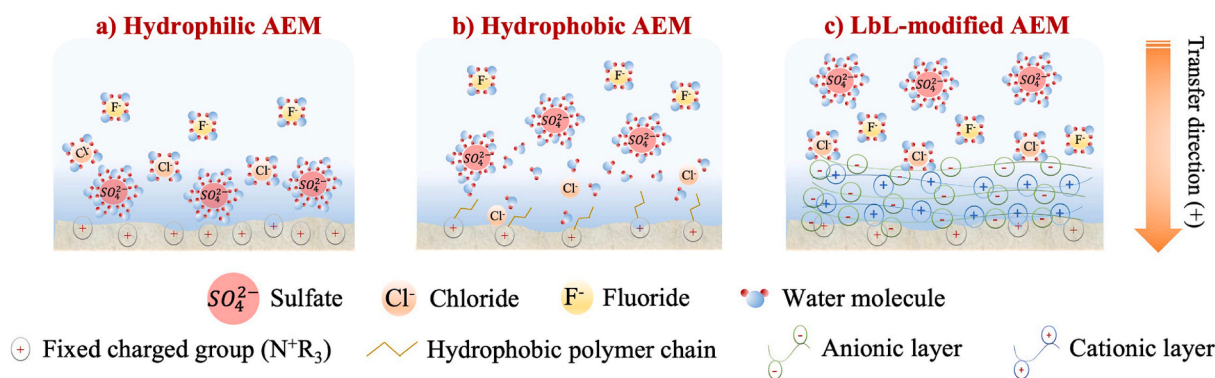


Fig. 11. Illustration depicting anion transport order: (a) hydrophilic AEMs enhance multivalent ion transport through higher electrostatic affinity; (b) hydrophobic AEMs impede ions with high hydration energy, which resist dehydration compared to ions with lower hydration energy; and (c) introduced dense anionic layers obstruct multivalent ion passage by intensifying electrostatic repulsion and size-exclusion effects [20].

Table 2
Membrane bulk phase with different alkyl chain structure and respective counter-ion selectivity performances in electrodialysis.

| Polymer backbone | Alkyl chain structure (n = length of alkyl chain) | Post treatment | WaterUptake (%) | IEC (meq/g) | Feeding solution (diluted cell) | Current density (mA·cm ⁻²) | Thickness (μm) | Resistance (Ω·cm ²) | Ion selectivity | | | Ref |
|---|---|----------------------|-----------------|-------------|--|--|----------------|---------------------------------|--|-------|---------|------|
| | | | | | | | | | ion pair | value | time | |
| PAEK | hexyl alkyl imidazolium salt-50 (n = 6)hexyl alkyl imidazolium salt-60 (n = 6) | – | 19 | 1.98 | 0.05 M | 5 | 110 | 4.98 | Cl ⁻ /SO ₄ ²⁻ | 6.74 | 30 min | [53] |
| | | | 24.9 | 2.15 | NaCl | | | | | 7.7 | | |
| PAES-NH ₂ | propyl alkyl imidazolium salt (n = 3)hexyl alkyl imidazolium salt (n = 6)nonyl alkyl imidazolium salt (n = 9)dodecyl alkyl imidazolium salt (n = 12) | – | 14 | 2.19 | 0.05 M | 5 | 110 | 2.1 | Cl ⁻ /SO ₄ ²⁻ | 3.4 | 30 min | [54] |
| | | | 13 | 2.01 | NaCl | | | | | 7.10 | | |
| | | | 9 | 1.84 | 0.05 M | | | | | 6.6 | | |
| | | | 8 | 1.69 | Na ₂ SO ₄ | | | | | 4.2 | | |
| BPPO | N,N-dimethylaminomethylpyridine-1-hexanol (n = 3)N,N-dimethylaminomethylpyridine-1-hexanol (n = 6)N,N-dimethylaminomethylpyridine-1undecanol (n = 11) | – | 53 | 0.48 | 0.05 M | 3.5 | – | 51.77 | Cl ⁻ /SO ₄ ²⁻ | 6.7 | 10 h | [55] |
| | | | 43 | 0.40 | NaCl | | | | | 9.3 | | |
| | | | 33 | 0.33 | 0.05 M | | | | | 13.1 | | |
| BPPO | Trimethylamine-0.75 (n = 1)N,N-dimethylhexadecylamine-0.75 (n = 16)N,N-dimethylhexadecylamine-0.75 (n = 16)N,N-dimethylhexadecylamine-0.5 (n = 16) | – | 23 | 1.8 | 0.05 M | 2.5 | – | 0.87 | Cl ⁻ /SO ₄ ²⁻ | 0.82 | 90 min | [56] |
| | | | 13 | 1.3 | NaCl | | | | | 5.02 | | |
| | | | 11 | 1.1 | 0.05 M | | | | | 7.58 | | |
| | | | 5 | 0.92 | Na ₂ SO ₄ | | | | | 12.8 | | |
| CMPSF | N,N-dimethylhexadecylamine-1 (n = 8)N,N-dimethylhexadecylamine-1 (n = 16)N,N-dimethylhexadecylamine-2 (n = 6) | – | 4.2 | 1.1 | 0.05 M | 2.5 | 95 | 53.6 | Cl ⁻ /SO ₄ ²⁻ | 35 | 90 min | [57] |
| | | | 3.5 | 1.1 | NaCl | | | | | 60.1 | | |
| | | | 5.7 | 1.32 | 0.05 M | | | | | < 5 | | |
| PAN-co-PnBA-co-PDMA | 1-bromoodecane (n = 10) | – | 18 | 1.6 | 0.01 M | 5.4–7.7 | 250–300 | – | Cl ⁻ /SO ₄ ²⁻ | 4.76 | – | [59] |
| | | | | | NaCl | | | | | | | |
| PAN-co-PVIm | 1-bromooctadecane (n = 18) | – | 22 | 1.03 | 0.05 M | – | 125 | – | Cl ⁻ /SO ₄ ²⁻ | 14.5 | – | [60] |
| | | | | | NaCl | | | | | | | |
| PAES (zwitter-ion) | hexyl alkyl imidazolium salt (n = 6) | UV | 15.1 | 1.77 | 0.05 M | 5 | 110 | 113.6 | Cl ⁻ /SO ₄ ²⁻ | 12.5 | 50 min | [61] |
| | | | | | NaCl | | | | | | | |
| PAES-NH ₂ + 15 %sPSF (zwitter-ion) | hexyl alkyl imidazolium salt (n = 6) | – | 19 | 1.52 | 0.05 M | 2.5 | 110 | 11.42 | Cl ⁻ /SO ₄ ²⁻ | 21.8 | 120 min | [62] |
| | | | | | NaCl | | | | | | | |
| BPPO | trimethylamine (n = 1) | Surface modification | 19 | 1.54 | 0.01 M | 10 | 86 | – | Cl ⁻ /SO ₄ ²⁻ F ⁻ /SO ₄ ²⁻ | 11.7 | 60 min | [20] |
| | | | | | NaCl | | | | | 8.3 | | |
| | | | | | 0.01 M NaF | | | | | | | |
| | | | | | 0.01 M Na ₂ SO ₄ | | | | | | | |

Nevertheless, it is important to highlight that the majority of research on hybrid membranes has primarily centered around selective CEMs. Utilizing the knowledge obtained from research on selective CEM studies can pave the way for advancements in AEMs, resulting in improved performance across diverse applications that involve monovalent anions.

Multilayer graphene-organic frameworks (MGOFs) are considered a new class of hybrid membranes, providing a tunable interlayer spacing through a layer of graphene oxide connected with a polymer material for the selective separation of monovalent ions in electro dialysis. Zhao et al. [64] designed an MGOF by coalescing quaternized PPO and graphene nanosheets grafted with sulfonated 4,4'-diaminodiphenyl sulfone (SDDS) for the selective separation of anions (Fig. 12). According to theory, the quaternary ammonium groups of the quaternized PPO are expected to graft with the sulfonic groups of the SDDS-graphene structure through either ion-dipole or hydrogen bond interactions, or in some cases, ionic bonding or other Coulomb interactions, leading to the coating of the membrane's surface. The selective separation between chloride and sulfate of the MGOF membranes was ascribed to the selective passage of monovalent ions through the independently grafted graphene in the MGOF. Additionally, the membrane exhibited low surface electric resistance ($2.79 \Omega\text{-cm}^2$). In a recent study, Ruan et al. [65] introduced a novel method involving MOF utilizing two distinct UiO-66 membranes with different degrees of sulfonation to effectively separate chloride ions from sulfate solution. The electro dialysis process demonstrated a remarkable monovalent selective separation rate of up to 36.23 for the chloride/sulfate system, with the increase of degree of sulfonation. The effects of pore size and charge repulsion are found to be crucial factors in enhancing ion selectivity.

Graphene, a typical two-dimensional carbon nanostructure, has been widely studied as graphene oxide sheets, which is another strategy for efficient ion sieving. Zhao et al. [66] developed anion channels for anion selectivity from sulfonated reduced graphene oxide nanosheets with negatively charged sulfonic acid groups. These nanosheets were synthesized via a facile distillation-precipitation polymerization followed by hydrazine reduction. Sulfanilic acid was grafted onto the graphene oxide sheets to separate each graphene oxide nanosheet. The selectivity between chloride and sulfate for the sulfonated reduced graphene oxide modified AEMs was determined to be 2.30. This was attributed to the greater electrostatic repulsion exerted by the sulfonic groups on the membrane surface towards divalent anions. The increase in the value of the membrane resistance was found to be only $0.66 \Omega\text{-cm}^2$. Subsequently, inspired by biological adhesion from mussels, the same group utilized sulfonated reduced graphene oxide to enhance the stability of sulfonated reduced graphene oxide nanosheets by polydopamine coating [67]. A commercial AEM modified by sulfonated reduced graphene oxide and polydopamine by means of electrostatics was investigated for the monovalent anion selectivity between chloride and sulfate. The selectivity of the sulfonated reduced graphene oxide-polydopamine membrane was 2.50 due to the synergistic effect of both electrostatic

repulsion and sieving effect during the 70-hour electro dialysis process.

More recently, another novel two-dimensional thin anion lamellar composite membrane was synthesized through the assembly of sulfonated $\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{STi}_3\text{C}_2\text{T}_x$) nanosheets onto a commercially available Nylon-66 microfiltration membrane that had been modified with QCS [68]. The integration of QCS modification provided continuous active sites, while the inclusion of ($\text{STi}_3\text{C}_2\text{T}_x$) lamellar ion channels imparted the membrane with enhanced electrostatic repulsion and ion steric effect, synergistically improving both flux and selectivity (Fig. 13). Specifically, the resulting two-dimensional thin anion lamellar composite membrane (N66-QCS/ $\text{STi}_3\text{C}_2\text{T}_x$) exhibited a chloride/sulfate selectivity of 14.67.

Another criterion for selecting an inorganic dopant is established based on considerations of charge density and stability. Cerium phosphate, a renowned cation exchanger, demonstrates the capacity to establish a stable anionic nitrate complex. In light of this, Golubenko et al. [69] developed hybrid membranes by integrating in situ synthesized cerium phosphate with a commercially available FujiFilm AEM Type I through ion exchange processes. The cerium phosphate was gradually distributed across the membrane thickness, facilitating the separation of chlorides and sulfates in electro dialysis. The resulting hybrid membranes exhibited a chloride/sulfate selectivity of 6.2. This enhanced selectivity was attributed to the formation of a narrow transport channel between the surface of the inorganic nanoparticle and the pore wall, leading to a decrease in sulfate transport due to the size-sieving effect.

3.1.2. Surface modification

Given the importance of selectively separating anions, the surface properties of AEMs are of utmost importance. Therefore, altering the surfaces of these membranes proves to be an efficient approach to affecting their capacity to separate ions. Surface modification can be achieved through various methods, including polyelectrolyte layer deposition, polymerization, and surface chemical reactions.

3.1.2.1. Layer-by-layer deposition. In the field of membrane surface modification, a widely used technique involves the application of polyelectrolyte layers onto the membrane surface through electrostatic attraction and simple immersion. This method utilizes a process known as LbL deposition, where alternating layers of oppositely charged polymers are sequentially applied [70]. Standard AEMs exhibit limited selectivity between ions of the same charge, while special-grade AEMs demonstrate insufficient selectivities for specific applications. To address this limitation, several research groups have turned to LbL deposition of polyelectrolytes on commercial AEMs as a means to enhance the monovalent selectivity of halide ions from sulfate-based solutions.

As an example, Mulyati et al. [71] demonstrated the selective behavior of commercial Neosepta AMX AEMs concerning competitive transport between chloride and sulfate ions by employing an alternating

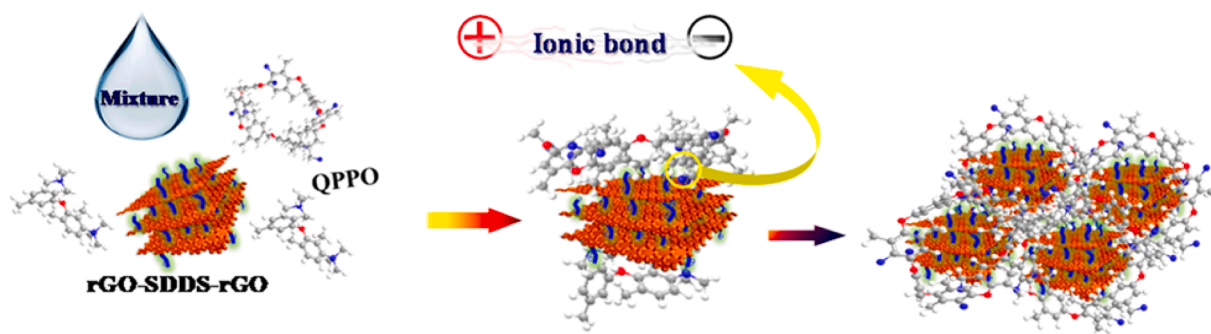


Fig. 12. Illustration depicting the synthetic route to the multilayer graphene-organic frameworks. The figure is reprinted with permission from [64] (Copyright © 2018, American Chemical Society).

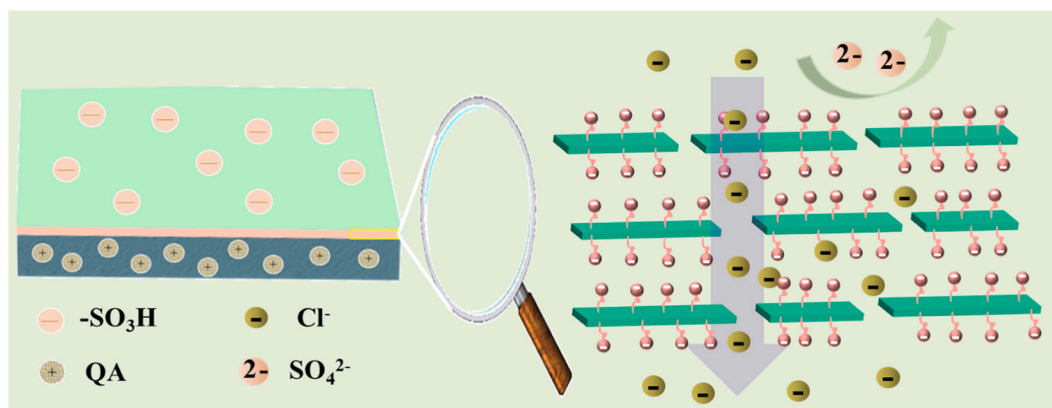


Fig. 13. Illustration depicting the separation of chloride from sulfate through developed AEM. The figure is reprinted with permission from [68] (Copyright © 2021, Elsevier).

LbL deposition of PSS and PAH layers. AEMs containing more than 15 layers, with an outermost PSS layer, exhibited a monovalent anion selectivity of 1.8. This selectivity was primarily attributed to the formation of a dense layer and the presence of a negatively charged surface, which impeded sulfate transport to some extent across the membrane. Ahmad et al. [72] utilized an identical polyelectrolyte pair but with different molecular weights of PAH to modify a commercial Fujifilm AEM under various deposition conditions in their investigation. The outcomes revealed enhancements in selectivity, reaching up to 7.4 for chloride/sulfate ions after 11 layers of polyelectrolyte deposition. This significant improvement in selectivity highlights the potential of employing diverse support materials and modification conditions to enhance the ion separation performance of the AEM.

It has been reported that a high deposition number of polyelectrolyte layers causes an increase in membrane resistance [73]. Zhang et al. [74] conducted an investigation where they introduced modifications to various commercial AEMs by employing poly(diallyldimethylammonium chloride) as the altered polycation in the presence of graphene. This approach led to the creation of graphene-incorporated polyelectrolyte layers, with the objective of reducing electrical resistance. This modification yielded notably enhanced chloride/sulfate selectivity ratios of up to 11 after 21 layers of polyelectrolyte deposition, a great improvement compared to the pristine AEM with a ratio of 4.5. The deposition process facilitated a steric hindrance effect, effectively restricting the passage of larger sulfate ions through the membrane. Moreover, a reduction in electrical resistance of

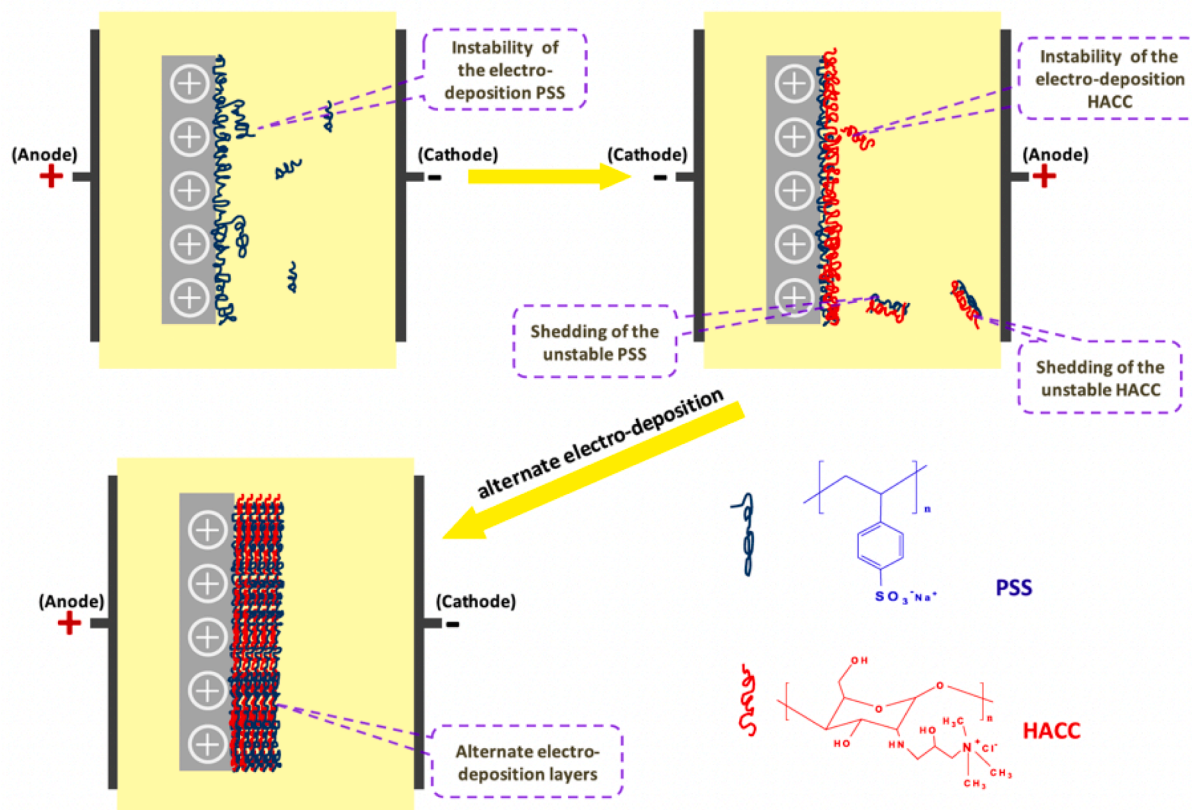


Fig. 14. Illustration depicting the application of the multilayered (PSS/HACC)_N alternate electro-deposition coating onto the surface of the membrane. The figure is reprinted with permission from [75] (Copyright © 2016, Elsevier).

the LbL modified membranes was observed, despite the considerable number of deposited layers. This reduction was attributed to the incorporation of conductive graphene material within the polyelectrolyte layer, which contributed to the improved electrical conductivity of the modified membrane. This study demonstrates the potential advantages of integrating graphene into polyelectrolyte layers, enhancing both ion selectivity and electrical properties of the AEM.

An alternative strategy to enhance ion selectivity while avoiding an increase in membrane resistance involves surface modification through electro-deposition, which has recently become a subject of significant interest. During the process of electro-deposition, a solution containing the desired modifier is exposed to an electrical field by applying electrical potential to the electrodes, facilitating the attraction and subsequent deposition of the oppositely charged modifier onto the membrane surface [23]. This controlled modification takes place within a specially designed cell, enabling precise and targeted surface alterations for improved ion selectivity.

In a study conducted by Zhao et al. [75], they performed surface modifications on a commercial AEM using adsorbed PSS and HACC (Fig. 14). After 90 min of electro-dialysis operation, they achieved an improved selectivity of up to 2.90 between chloride and sulfate ions,

alongside an electrical resistance value of $4.52 \Omega\text{-cm}^2$. Subsequently, they developed a monovalent AEM by incorporating polydopamine as both the innermost and outermost layers [76]. This was combined with N-O-sulfonic acid benzyl chitosan (NSBC), building upon the concept of a “three-layer” structure. As a result of this modification, they achieved a selectivity of 2.20 between chloride and sulfate, surpassing that of the commercial membrane (0.78). The area resistance for the modified membrane increased by only $0.08 \Omega\text{-cm}^2$. Compared to static coating, an important advantage of the electro-deposition approach is the reduction in ionic resistance observed in the modified membranes. This characteristic renders electro-deposition an appealing method for membrane surface modification.

To achieve a more uniform and homogenous deposition of layers, Zhao et al. [77] employed electric pulses, in which the polarity of the electrodes alternates rapidly and intermittently, thereby driving the charged layers onto the unmodified membrane surface. By coating a commercial AEM membrane with 7.5 bilayers of NSBC and HACC, a remarkable selectivity of 47 between chloride and sulfate ions was achieved while maintaining a low membrane resistance value of $4.25 \Omega\text{-cm}^2$. In their recent investigation, the application of alternating current LbL deposition technique to develop durable multilayer AEMs was

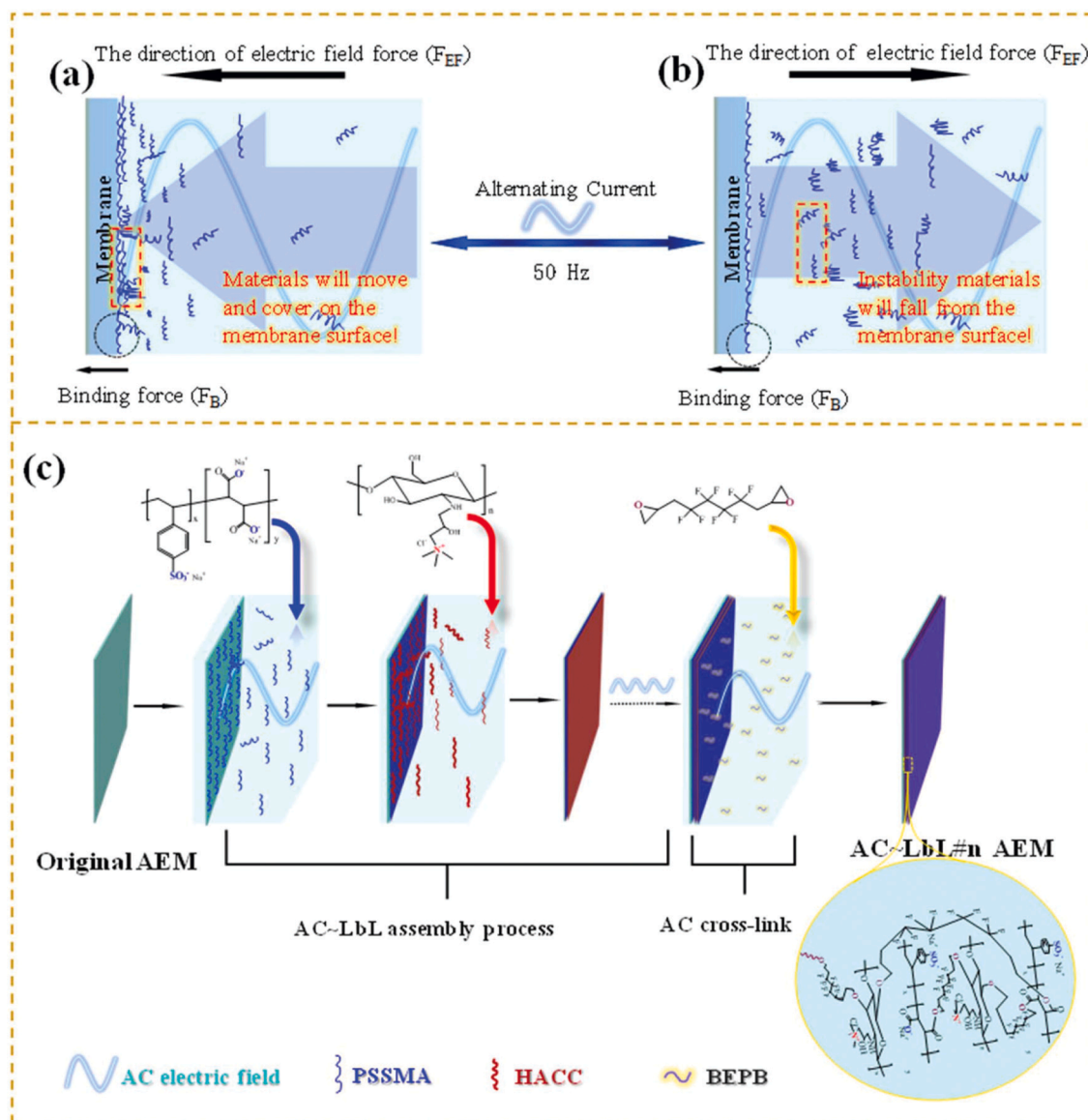


Fig. 15. Illustration depicting the utilization of alternating current LbL technique. The figure is reprinted with permission from [78] (Copyright © 2019, RSC Pub).

explored [78]. This involved alternately coating the membrane with hydrophilic, negatively charged sodium salt of poly(4-styrenesulfonic acid-co-maleic acid) and positively charged HACC, followed by cross-linking, as depicted in Fig. 15. The resultant modified AEMs exhibited a chloride/sulfate selectivity of 4.9, which stabilized at approximately 4.52 even after continuous operation for 96 h. The use of alternating current for depositing polyelectrolyte layers on a membrane offers advantages in terms of precise control, uniformity, reduced fouling, and improved layer structure. This innovative approach holds great promise in enhancing the selectivity and long-term stability of AEMs for various practical applications.

In order to enhance the controllability and interface homogeneity of the modification process while ensuring the long-term reliability of the deposited functional layers, Zhang et al. [79] adopted a novel synergistic approach. They utilized a combination of in-situ chemical nucleophilic substitution reaction and electro-deposition using alternating current to fabricate a monovalent anion selective membrane (Fig. 16). Commercial AMX membrane served as the substrate, onto which a pre-deposition step of polydopamine and chitosan was performed to facilitate co-deposition on the pristine membrane. Subsequently, reactive blue 4 was selected as the functional material and subjected to electrical deposition, thereby enhancing the chemical reactivity. The synergistic method significantly reinforced the ion sieving process by introducing counter-charged layers, leading to a chloride/sulfate selectivity of 11.85, whereas the membrane's resistance was found to be $21.39 \Omega \cdot \text{cm}^2$.

The electro-deposition method applying alternating current was also explored for the separation of another halide anion, bromide, from sulfate ions. In a recent study, Lan et al. [80] investigated the surface modification of tailor-made AEMs synthesized through a chemical substitution reaction between BPPO and 4-hydroxy-1-methylpiperidine. Subsequently, a negatively charged layer was assembled on the membrane's surface using 4,4'-diaminostilbene-2,2'-disulfonic acid. The resulting membrane exhibited a selectivity of 12.6 between bromide and sulfate ions, surpassing even that of the utilized commercial ASE membrane in electro dialysis. This study proposes innovative concepts for creating a membrane with a focus on bromide selectivity, aiming to enhance resource recovery.

3.1.2.2. Surface polymerization and chemical reaction. Surface

polymerization of specific macromolecules onto an AEM represents a viable approach to introduce a selective layer on its surface, thereby achieving the intended selectivity. Dopamine, for instance, undergoes oxidation in an alkaline aqueous solution and forms strong adhesive interactions with surfaces, reminiscent of the adhesive properties found in mussel proteins. Taking advantage of this bio-inspired coating strategy, Ruan et al. [81] prepared a negatively charged mono-selective AEM through sulfonated dopamine. By introducing high reverse charges and a dense separation layer on a commercial membrane, the modified AEM exhibited a selectivity of up to 34.02 when tested for the separation of chloride from sulfate ions, attributed to the synergistic effect of sieving and electrostatic repulsion. This selectivity far surpassed that of the pristine membrane, which showed a selectivity of 1.0, and the dopamine-modified membrane, which displayed a selectivity of 11.59. Furthermore, the modified membrane demonstrated stability during 90 h of electro dialysis operation. However, a fourfold increase in surface resistance was observed through the sulfonated dopamine-modified membrane.

Chemical modification of membrane surfaces with various functional groups is another attractive method to introduce desired surface properties. This might include photo-induced immobilization, diazonium-induced anchoring, and the formation of sulfonamides. For instance, Liu et al. [82] utilized the photosensitive DAS to photo-cross-link the membrane surface, enhancing the selectivity and durability of the membranes, as depicted in Fig. 17. Through this modification, they achieved a monovalent anion selectivity of 4.4 between chloride and sulfate ions during a 76-hour electro dialysis experiment. Subsequently, a commercial AEM was modified by infiltrating and immobilizing a negatively charged layer of a photosensitive DAS solution to create a membrane with an enhanced selectivity of 11.2 during over 80 h of electro dialysis [83]. Notably, the modified membrane exhibited low ionic resistance of $4.5 \Omega \cdot \text{cm}^2$, making it a promising candidate in practical applications.

Amide condensation has emerged as a viable strategy for membrane functionalization. Membranes coated with L-3,4-dihydroxyphenylalanine (L-Dopa) can offer the advantage of forming highly stable covalent bonding with amine-containing compounds. In a study conducted by Zhao et al. [84], they fabricated AEMs with enhanced monovalent anion selectivity through the self-polymerization and

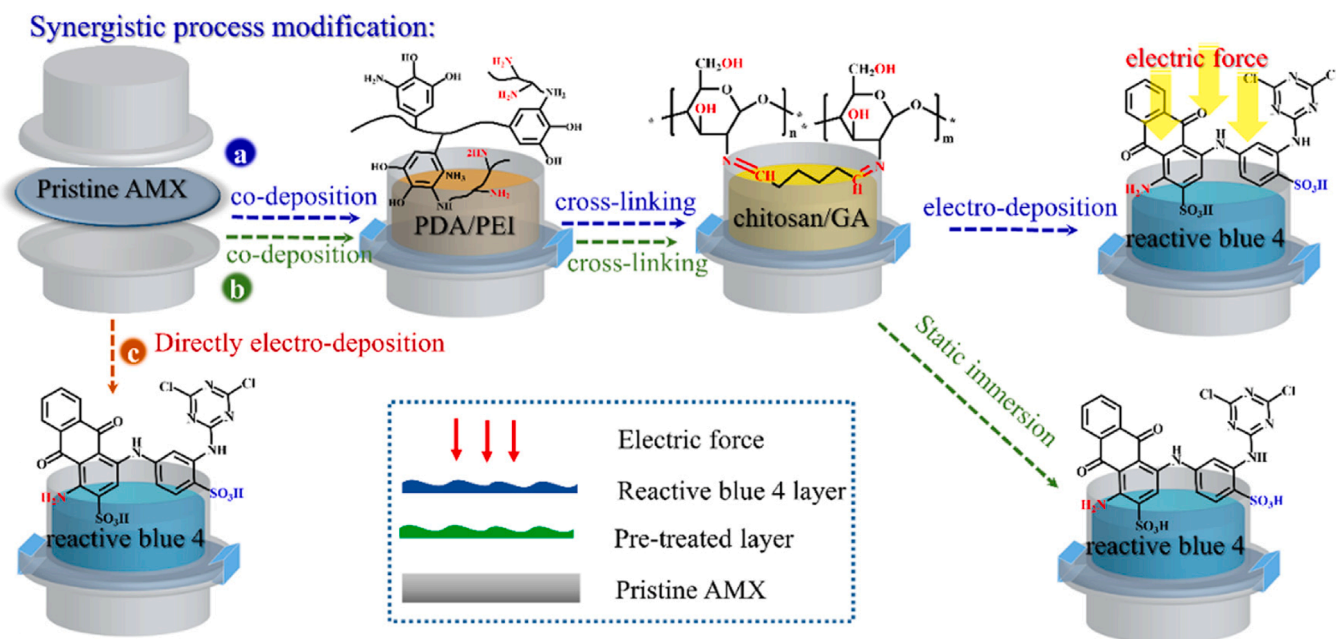


Fig. 16. Illustration depicting three distinct approaches: (a) synergistic process modification; (b) static surface chemical modification; (c) physical electro-deposition to prepare anion monovalent selective membranes. The figure is reprinted with permission from [79] (Copyright © 2021, Elsevier).

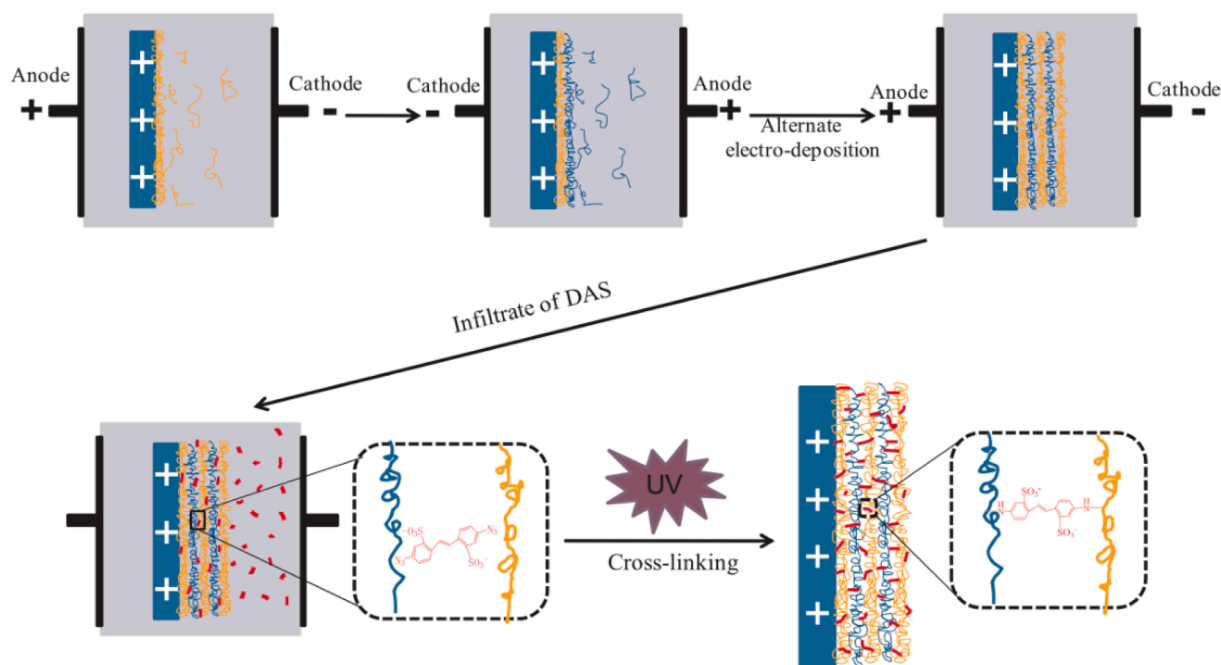


Fig. 17. Illustration depicting the modification of cross-linked electro-deposition multilayer membranes. The figure is reprinted with permission from [82] (Copyright © 2017, Elsevier).

amidization of L-Dopa with sodium 4-amino-benzenesulfonate. The resulting AEM, featuring a negatively charged thin layer, exhibited a monovalent anion selectivity of 5.29 (bromide/sulfate) and 4.66 (chloride/sulfate), whereas the original AEM demonstrated significantly lower selectivities of 1.22 and 1.00, respectively. Additionally, the

modified AEM demonstrated a low ionic membrane resistance of 2.12 $\Omega \cdot \text{cm}^2$. In a separate investigation, Lejarazu et al. [85] prepared monovalent selective AEMs using a two-step modification process, leveraging mussel-inspired surface chemistry and amino condensation. The subsequent application of an alternating current field further

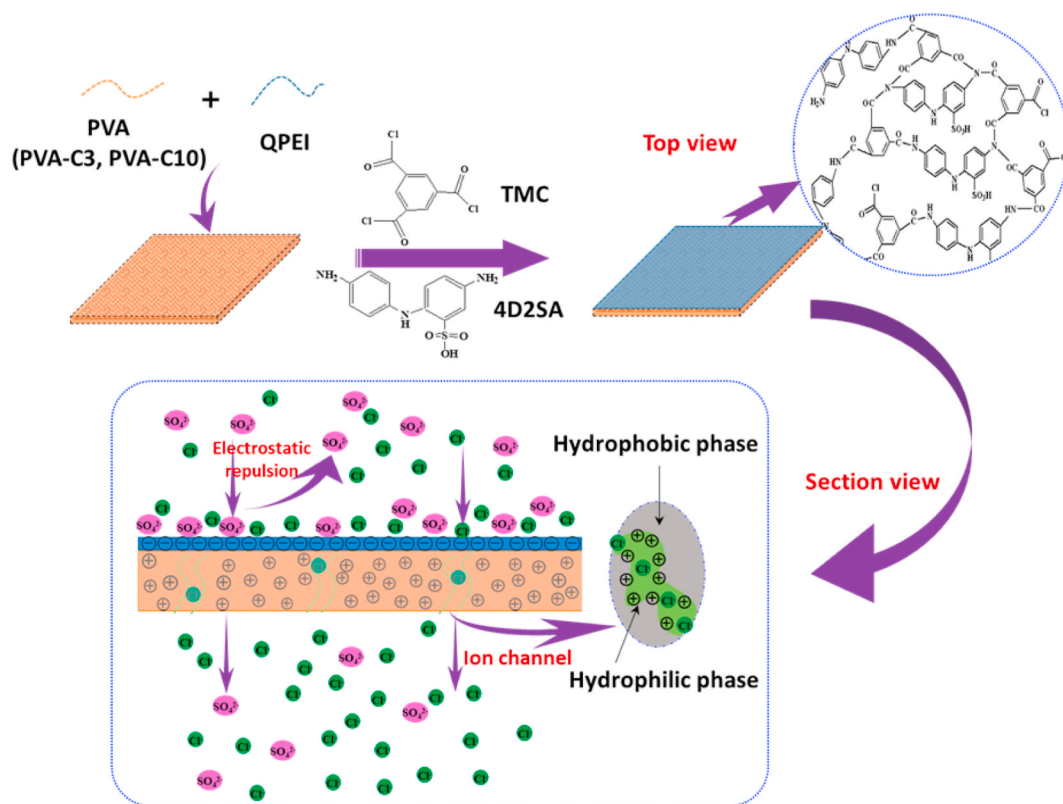


Fig. 18. Illustration depicting the preparation process for monovalent selective AEMs through interfacial polymerization. The figure is reprinted with permission from [87] (Copyright © 2021, Elsevier).

enhanced the homogeneity and stability of the coating. The process began with the deposition of L-Dopa on the surface of an AMX membrane, followed by the chemical attachment of 4,4'-diamino-2,2'-biphenyldisulfonic acid through an amide condensation reaction facilitated by the application of an alternating current (15 V at 50 Hz). Desalination analyses demonstrated an increase in the selective separation of chloride over sulfate, rising from 1.25 in the original membrane to 2.13 after 60 min of desalination. Notably, the resulting AEM displayed a membrane resistance of $3.6 \Omega\text{-cm}^2$.

Interfacial polymerization represents a highly effective and versatile approach for creating thin covalently-bonded layers on membrane surfaces. In a study by Zhang et al. [86], monovalent anion selective membranes were prepared through interfacial polymerization of a benzene-rich monomer and cross-linker trimesoyl chloride on the polyvinyl alcohol-quaternized chitosan (QCS) blend membrane. The reaction between the $-\text{COCl}$ groups of trimesoyl chloride and $-\text{NH}/-\text{OH}$ groups on the membrane's surface facilitated the formation of strong covalent bonds. The introduction of the thin electronegative layer resulted in a substantial increase in chloride selectivity over sulfate, elevating it from 1.8 to 10.3. Furthermore, this selectivity remained stable during a 10-hour electro dialysis operation, highlighting the efficiency and durability of the modified membrane. In a more recent investigation, Li et al. [87] fabricated a series of polyvinyl alcohol-based monovalent anion selective membranes using interfacial polymerization of 4,4'-diaminodiphenylamine-2'-sulfonic acid and trimesoyl chloride to deposit a thin electronegative layer with a loose structure on the membrane surface (Fig. 18). The study revealed that membranes with the longest hydrophobic alkyl side chain and the highest concentration of 4,4'-diaminodiphenylamine-2'-sulfonic acid exhibited a selectivity value of 6.3, while the membrane resistance was found to be $5.1 \Omega\text{-cm}^2$. More recently, Afsar et al. [88] developed anion selective membranes via in-situ interfacial polymerization technique on methyl diethanolamine quaternized membranes. The approach simplifies synthesis, avoids external monomers, and produces highly selective membranes compared to the conventional interfacial polymerization process. The resultant membranes exhibit an impressive selectivity of 59.5 for chloride/sulfate system, along with a low membrane resistance of $4.7 \Omega\text{-cm}^2$.

An additional covalent bonding strategy involves the preparation of a chemically bound carboxylic polymer layer containing quaternary amine and carboxyl groups [89]. The synthesis scheme (Fig. 19) illustrates the application of the Menshutkin reaction, wherein a tertiary amine on a copolymer reacts with the bromomethyl group within the membrane to create a surface functional layer. Subsequent hydrolysis leads to the generation of an abundance of carboxyl groups on the

surface layer, which in turn facilitates the selective permeation of monovalent anions. The resultant membrane, characterized by the highest surface content of carboxyl groups and the densest polymer layer, exhibited a selectivity value of 7.31 between chloride and sulfate ions, which was found to be two times higher compared to commercial Neosepta ACS AEM.

3.2. Process-controlled selectivity in electro dialysis

3.2.1. Optimizing operating conditions

Ion selectivity is also a function of various process conditions, such as current density, solution composition, flow rate, pH and stack design as well as membrane properties. As a result of the flow of faradaic current between a pair of electrodes in the electro dialysis unit, boundary layers form at the membrane-solution interfaces, where counter-ion concentrations decrease towards the diluate compartments and increase towards the concentrate compartment. The thickness of the boundary layer can change based on the operating conditions, affecting the transport rate of ions to the membrane's surface.

Current density is a crucial operating parameter that has a significant impact on ion selectivity. Under conditions of underlimiting current densities, ion selectivity is dictated by the transport rate of competing ions within the membrane. Conversely, in situations involving overlimiting current densities, ion selectivity is primarily influenced by the transport properties of ions within the boundary layer. For instance, Golubenko et al. [69] reported that when treating 1:1 mixtures of sodium sulfate and sodium chloride with a monovalent selective AEM, the selectivity between chloride and sulfate ions increased with the current density under membrane-diffusion controlled conditions, favoring the transport rate of chloride ions. The selectivity of 6.4 was achieved when operating at limiting current density conditions. In addition to the influence of current density, pH also exerts a substantial impact on the selective separation of ions. Zhang [90] documented a positive effect of higher pH levels on the efficiency of separating monovalent and multivalent ions using monovalent selective AEMs. The selectivity between chloride and sulfate ions showed improvement as the pH transitioned from neutral to 9. This phenomenon was attributed to changes in the surface charge of the AEM, which tended to become less positively charged. Nevertheless, their study indicated that reducing the current density is more effective in enhancing membrane selectivity than increasing pH.

Other investigations conducted to separate chloride from sulfate ions involved using a specialized electro dialysis arrangement referred to as "selectrodialysis" [91]. The aim of the selectrodialysis setup is the

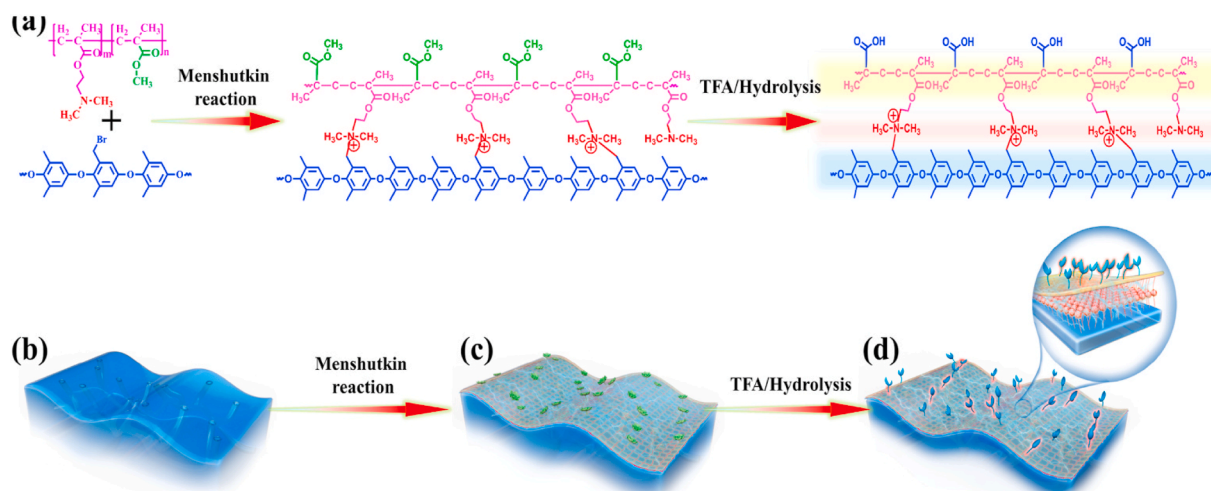


Fig. 19. Illustration depicting the route for the synthesis of monovalent selective AEM. The figure is reprinted with permission from [89] (Copyright © 2020, Elsevier).

fractionation between counter-ions of different valency simultaneously to desalinating the feed solution. The design of electrodialysis builds upon the principles of conventional electrodialysis, involving the incorporation of one or more specialized membranes between standard AEMs and CEMs (Fig. 20). During electrodialysis, three major effects occur: (1) the feed stream between the CEM and AEM gets desalinated, (2) the multivalent ion concentration in the product stream between the AEM and the monovalent selective AEM increases, and (3) the brine between the monovalent selective AEM and CEM gets more concentrated in ions. Consequently, the feed solution is desalinated while the product stream is fractionated, meaning that the multivalent ions are collected in a separate product stream. Zhang et al. [91] used electrodialysis for separating sulfate from a mixture of sodium sulfate and sodium chloride, investigating the influence of modifying the pH and current density on the selectivity of the stack. For an equimolar feed of sodium sulfate and sodium chloride, a purity of the sulfate product stream of 85 % was achieved at a current efficiency above 50 %. The observed impact of lower current ($31.2 \text{ A}\cdot\text{m}^{-2}$) is linked to the diminished movement of ions through the membrane, particularly affecting the flow of larger multivalent ions more significantly than monovalent ions. Moreover, the outcomes of the study demonstrated that elevating the pH of the solution from 6 to 10 at a lower current density resulted in increase of sulfate purity by 27 %, yielding an enhancement of selectivity. This effect can be attributed to the enhanced selectivity exhibited by the monovalent selective AEM at elevated pH levels. The influence of heightened pH on ion selectivity is attributed to the reduction in the positive surface charge of the AEM, which subsequently affects the electrostatic attraction forces between ions and the membrane surface.

In a recent study, Cui et al. [92] also investigated the separation and concentration of chloride and sulfate ions using synthetic wastewaters in electrodialysis. The objective of using electrodialysis was to achieve the separation and enrichment of monovalent/divalent ions while also retaining organic compounds for a zero-liquid discharge process. They examined the impact of initial sodium chloride concentration in the product solution, applied current density, and feed composition on transport mechanisms. Notably, a sulfate purity of 92.3 % was achieved in the product solution with an initial product concentration of 25 wt% sodium chloride. Additionally, optimal salt concentration and purity were obtained at a moderate current density ($200 \text{ A}\cdot\text{m}^{-2}$). The study also affirmed that the presence of organic compounds in the feed contributed to producing high-quality salts, with sodium sulfate reaching 94.8 % purity and sodium chloride achieving 91.6 % purity.

If the objective of the electrodialysis process is the mere fractionation

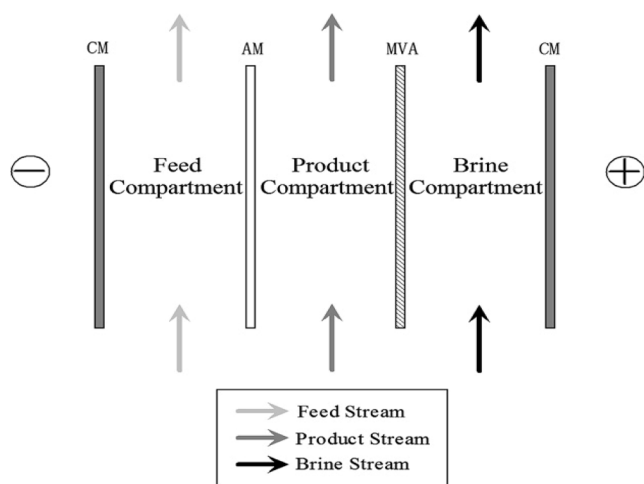


Fig. 20. Illustration depicting the basic configuration of a electrodialysis stack to fractionate anions, where CM indicates a cation exchange membrane, AM stands for AEM, and MVA for monovalent selective AEM. The figure is reprinted with permission from [91] (Copyright © 2012, Elsevier).

between monovalent and multivalent anions, the CEMs can be removed from the electrodialysis setup, resulting in a stack with alternating selective and non-selective AEMs (Fig. 21). In such setup, monovalent anions permeate both AEMs, while multivalent anions are held back by the selective AEMs, and cations do not permeate at all. The result is a decreased concentration of monovalent ions and increased concentration of multivalent ions in every second compartment, and *vice versa* for every other compartment. Overall, the multivalent ions in one compartment are exchanged by monovalent ions. This concept was proposed by Galama et al. [93], and given the name “fractioning electrodialysis”. The setup was tested for separation of sulfate and chloride from ternary mixtures mimicking seawater concentrations. The degree of fractionation between chloride and sulfate increased with the current density, and reached a maximum value of 60 %. The coulombic efficiency decreased rapidly during the electrodialysis process, leading to relatively high volumetric energy consumption. It was argued that the main reason for the low coulombic efficiency was the significant difference in concentration of chloride and sulfate, alongside with co-ion transport, a lack of membrane selectivity, and backdiffusion of water.

Until now, most endeavors have primarily concentrated on the separation of chloride from solutions. However, the significance of removing fluoride from effluent streams is comparable to that of chloride removal. The utilization of tailor-made membranes for this separation, as proposed by existing literature, often encounters limitations. The removal of fluoride is primarily documented through the application of commercially available monovalent selective AEMs under different operating conditions. Kabay et al. [94] conducted an investigation focused on the selective separation of fluoride from a ternary mixture involving chloride and sulfate through the application of electrodialysis. The initial mixture comprised an equimolar composition with an initial fluoride concentration of $100 \text{ mg}\cdot\text{L}^{-1}$. Their study demonstrated an increased separation efficacy proportional to increased initial fluoride concentrations in the feed solution. Furthermore, heightened applied potentials correlated positively with elevated percentages of fluoride removal. The sequence of ion migration was established as chloride > fluoride > sulfate. The presence of chloride was identified as an influencing factor on fluoride separation, unlike sulfate ions. Subsequently, Arar et al. [95] investigated the separation of lower fluoride concentrations ($2 \text{ mg}\cdot\text{L}^{-1}$) from mixtures in a 1:25:25 ratio featuring chloride and sulfate. The electrodialysis process was operated at 80 % of the limiting current density of the mixture. Their investigation revealed a high fluoride removal rate (96 %) in the

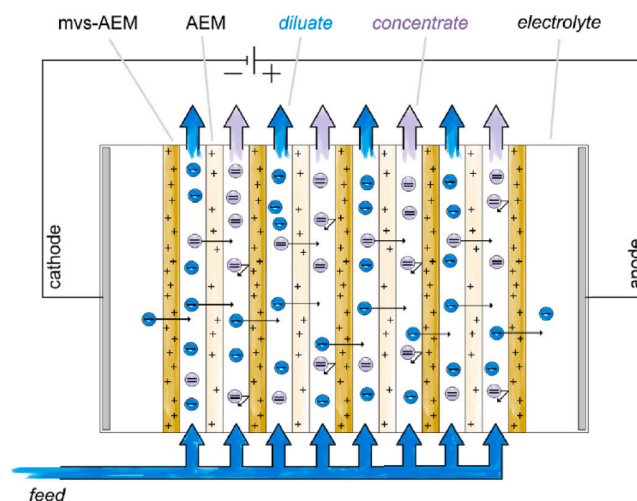


Fig. 21. Illustration of a fractioning electrodialysis stack, where common AEMs and monovalent selective AEMs are alternated to fractionate monovalent and multivalent anions (mvs-AEM – monovalent selective AEM). The figure is reprinted with permission from [93] (Copyright © 2016, Elsevier).

presence of both chloride and sulfate. In contrast, binary fluoride and chloride mixtures exhibited a 63 % fluoride removal rate, while fluoride and sulfate mixtures demonstrated a 93 % removal rate. This was attributed to the enhanced ionic strength stemming from the presence of both chloride and sulfate. Importantly, a similar enhancing effect was noted concerning the leakage of chloride and sulfate ions, whose removal rates reached 98 % and 53 %, respectively.

More recently, a study by Luo et al. [1] highlighted the application of electro dialysis in separating fluoride and chloride ions from an ammonia-based flue gas desulfurization slurry. They employed a two-stage electro dialysis process and investigated the effects of applied voltage, circular flow rate, and solution pH on ion movement. Generally, higher applied voltage and flow rate led to increased transport of halide ions. However, excessively high circular flow rates resulted in shorter ion retention time on the membrane surface, reducing the chances of ions adhering and binding to the membrane. Furthermore, while chloride migration remained unaffected by pH, fluoride migration was notably influenced. The most effective fluoride migration occurred within a pH range of 4–6. In terms of purity, the solution containing chloride reached a maximum purity of 98.6 %, whereas the fluoride-containing solution achieved a purity of 51.4 %.

Recently, Zimmermann et al. [19] explored the idea of utilizing the specific limiting current density of target ions in multi-ionic mixture to provoke favorable mass transport of these ions, resulting in higher separation efficiencies. For 1:1:100 mixtures of fluoride, chloride, and sulfate, the best performance was observed when operating electro dialysis at the limiting current density for chloride and fluoride ($130 \text{ A}\cdot\text{m}^{-2}$), leading to complete depletion of chloride after 90 min and of fluoride after 300 min while sulfate leakage was 20 %. The effectiveness of separating fluoride from sulfate exhibited a noteworthy increase when elevating the current density from $100 \text{ A}\cdot\text{m}^{-2}$ to $130 \text{ A}\cdot\text{m}^{-2}$. However, efficiency decreased again when reaching $200 \text{ A}\cdot\text{m}^{-2}$. Consequently, operating electro dialysis in alignment with the limiting current density of the target ion yielded superior selectivity compared to employing higher or lower current densities.

Overall, the investigated studies render that the competitive transport of counter-ions in electro dialysis is governed by a complex interplay of multiple influencing factors. In particular, the flow rate plays a pivotal role in shaping the boundary layer thickness at the membrane surface. At lower flow rates, a thicker boundary layer is developed. In contrast, higher flow rates promote enhanced fluid mixing, leading to more thorough solution homogenization and the consequent reduction in the thickness of the boundary layer. Hence, at higher flow rates, the diffusion of the ions in the boundary layer has less impact on the selectivity. The composition of the solution, particularly the types and quantities of ions, profoundly influences ion selectivity owing to their diverse physical properties because ion movement and interaction relies on their charge, size, and concentration in fluid dynamics. A solution containing an array of ions with distinct characteristics experiences their behavior influenced by these inherent properties. For instance, smaller monovalent ions exhibit swifter movement in solution due to their reduced size and weaker electrostatic interactions compared to larger or multivalently charged ions. Consequently, the composition of ions significantly impacts their transport, diffusivity, and migration rates within the solution. Additionally, solution pH has an influential effect by altering the ionization of functional groups on the membrane surface. pH fluctuations can modify the charge state of the membrane surface, thereby impacting the interactions between ions and the membrane, consequently shaping the characteristics of the boundary layer and ion transport. Furthermore, higher solution concentrations intensify ion competition near the membrane surface. This heightened competition can substantially affect the boundary layer by influencing the rate at which ions approach and interact with the membrane, potentially altering selectivity and the thickness of the boundary layer.

The meticulous control of these parameters stands as a fundamental requisite in comprehending the influence of these factors on ion

transport, interactions, and distribution within the solution, all while mitigating their impact on the boundary layer in electro dialysis. Through the maintenance of optimal conditions, including the avoidance of excessive ion concentrations, pH regulation, and precise control of the flow rate, it becomes feasible to modulate the thickness and properties of the boundary layer. This deliberate regulation serves to enhance the selectivity of the ion exchange process in electro dialysis, ensuring enhanced separation and purification of ions.

3.2.2. Case studies with real industrial solutions

Industrial applications involving the removal of halide ions from sulfate solutions have been addressed through the utilization of AEMs in conjunction with selective electro dialysis technology. These applications encompass a range of sources including groundwater, brines generated from chemical industry processes, concentrate generated from reverse osmosis, and effluents originating from hydrometallurgical operations.

One of the investigations was carried out focusing on the valorization of brines originating from chemical industry processes [96]. In this study, they aimed to achieve the separation of chloride and sulfate using IEM technology through the selectro dialysis process (Fig. 22). The research involved testing various initial electrolytes and different concentration levels to optimize the efficiency of separation, employing a monovalent selective AEM. The most optimal outcome emerged when utilizing an initial sodium chloride solution in both the brine and product compartments, with a concentration twice that of the brine feed. This process resulted in purities of over 90 % for sulfate in the divalent-rich stream and around 90 % for chloride in the monovalent-rich stream.

Real solution investigations also involved the separation of multiple halide ions from process streams, with a specific focus on water purification and reuse purposes. Ergun et al. [97] conducted a study on the removal of fluoride from a real water sample taken from Kizildere (Kütahya, Turkey), where chloride and sulfate ions were found to be more than 3 and 40 times concentrated than fluoride. The investigation involved the use of SB-6407 AEM to process the real water solution. This was carried out subsequent to determining the optimal pH of the feed phase (pH 6) and the applied current density ($8.48 \text{ mA}\cdot\text{cm}^{-2}$) through experimentation with a model solution in electro dialysis. Defluorination of real water was achieved, reducing the fluoride concentration from $20.6 \text{ mg}\cdot\text{L}^{-1}$ to $0.84 \text{ mg}\cdot\text{L}^{-1}$ (96 % reduction) over a duration of 120 min of electro dialysis. This achievement was attained despite the presence of high levels of chloride and sulfate ions in the actual water sample.

In another study, electro dialysis with selective membranes was employed to remove arsenic and monovalent ions from brackish water reverse osmosis concentrate [98]. The selective AEMs exhibited high selectivity in removing monovalent anions (chloride, fluoride, bromide, nitrate) over divalent anions (sulfate, phosphate) at a wide range of current densities (55 to $323 \text{ A}\cdot\text{m}^{-2}$). In accordance with its favorable mass transport characteristics, the removal selectivity of chloride was consistently higher than that of fluoride. The overall salt concentration reduction was the highest at currents around the limiting value, while the normalized salt removal rate in terms of mass of salt per membrane area and applied energy was highest at lower current densities. This was attributed to a decrease in energy efficiency at elevated current densities. Electro dialysis was successfully employed to selectively remove monovalent anions including halides from reverse osmosis concentrate.

The research endeavors also extended to investigating halide removal from a variety of distinct sources. Xiao et al. [99] investigated different practical cases involving the removal of halide ions from spent zinc sulfate electrolytes within a hydrometallurgical circuit. They employed a standard TWDDA AEM for this purpose. The real composition of the spent electrolyte consisted of various elements in ionic forms, including zinc, magnesium, manganese, hydrogen, sodium, potassium, sulfate, chloride, and fluoride, each present in distinct quantities. Notably, the sulfate concentration was approximately 670 times higher than chloride and 3000 times higher than fluoride. The results of the

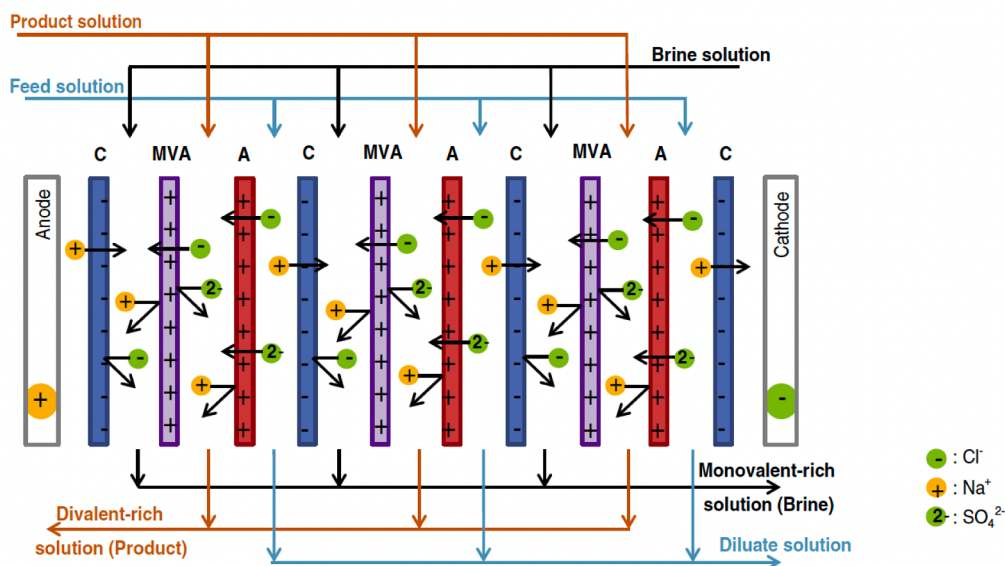


Fig. 22. Illustration depicting the selectrodialysis stack with membrane arrangement. (C – CEM, MVA – monovalent selective AEM, A – AEM). The figure is reprinted with permission from [96] (Copyright © 2016, Elsevier).

investigation revealed removal efficiencies of 50–70 % for chloride and 30–42 % for fluoride, while sulfate leakage was approximately 22.5 %. Remarkably, the zinc loss during the process was minimal, accounting for less than 1 % of the overall content. Moreover, the purification cost was normalized to around \$3.49 per cubic meter of the spent electrolyte. This approach demonstrated greater cost-effectiveness compared to the current methods involving CuCl.

Ball et al. [100] conducted an extensive study on the purification of zinc sulfate electrolytes from hydrometallurgical streams, encompassing halide ions like chloride and fluoride, through electrodialysis. The zinc sulfate electrolyte solution contained 150 mg·L⁻¹ of chloride, 50 mg·L⁻¹ of fluoride, and a sulfate concentration of 300 g·L⁻¹. The approach involved adjusting various parameters such as current density, pH, flow rate, AEM type, and electrolyte solution concentration. By selecting optimal conditions, the proposed method demonstrated the capability to achieve effective removal of halide ions from the zinc sulfate electrolyte. Specifically, through this approach, a significant removal rate of 87 % for chloride and 56 % for fluoride was achieved in one or more stages of the process. This study thus represented the potential for efficient purification of zinc sulfate electrolyte, with a focus on halide ions removal, by strategically manipulating the relevant variables.

4. Challenges and perspectives

Customized AEMs and optimization of operating conditions for removing halide ions from solutions rich in sulfates show promising results in electrodialysis applications. However, it is important to note that several challenges are likely to emerge and require careful consideration. For instance, limited information is available regarding the selectivity of fluoride over sulfate with developed AEMs in electrodialysis. Most studies have relied on commercially available single-ion selective AEMs. However, existing commercial AEMs lack the desired ability to selectively separate fluoride ions from sulfate solutions. As a result, there is a significant need to implement efforts into designing AEMs with tailored characteristics to effectively remove fluoride from sulfate-rich solutions.

Moreover, it is crucial to address gaps in our understanding concerning the impacts of solution composition, particularly in the context of counter-ion selectivity. There is a distinct lack of research regarding the feasibility of separating trace amounts of halide ions from highly concentrated sulfate solutions within complex mixtures containing

multiple ions, which is a prevalent scenario in industrial processes. While theoretical models and laboratory experiments provide valuable insights into ion transport mechanisms, the complexities introduced by the presence of mixtures of multiple ions in practical applications cannot be ignored. Hence, it is significant to explore the competitive effects of the high concentration of sulfate ions in the solution on the efficiency of halide removal.

Furthermore, a comprehensive understanding of how co-ions affect the migration of halide ions is pivotal for designing more efficient and optimized ionic systems. Conducting comprehensive research involving real solutions is essential, as real-world solutions encountered in industrial and environmental contexts rarely consist of single ion species. Instead, they often comprise diverse combinations of ions with varying charges, sizes, and chemical behaviors. Consequently, investigating the intricate interplay between co-ions and their impact on the transport of halide ions is of paramount importance.

There is also a notable lack of investigation into membrane scaling, fouling, and active layer degradation. Industrial solutions can contain various impurities, including particulates and organic matter, which diminish transport efficiency and increase energy consumption. This, in turn, not only reduces selectivity performance but also adversely affects the long-term operation of the electrodialysis process. As a result, there exists an urgent need for in-depth investigations to enhance the long-term stability of the modified AEMs. This must be achieved while avoiding an increase in membrane surface resistance and preserving high ion selectivity. It is crucial to develop effective methods for regenerating or cleaning the membranes in order to maintain their performance and extend their lifespan.

Lastly, the impact of operational factors like temperature, pH, rinse solution, and stack size has not received significant attention in the realm of electrodialysis with selective ion separation. Additionally, given the interplay between ion selectivity, solution characteristics, and process conditions, it is crucial to employ comprehensive and suitable modeling techniques to determine the optimal configuration for specific electrodialysis applications. Although attempts have been made to model electrodialysis systems, the Nernst-Planck approach stands out as the most established one. Nonetheless, the modeling of scenarios involving competing counter-ions remains limited. There is a clear requirement and opportunity for a more systematic exploration of operational conditions facilitated by advanced modeling tools in furthering this research area. Accounting for flux-force coupling using

Onsager reciprocal coefficients is also important for water balance and energy accounting in a systems perspective.

5. Conclusions

Utilizing AEMs within the electro dialysis process involves selectively eliminating undesired components from operational streams. Conventional AEMs can accomplish this objective partially; however, their capability to effectively separate counter-ions remains restricted. Progress in developing AEM materials, coupled with enhancements in the design of electro dialysis processes, has facilitated overcoming the limitation of ion selectivity and significantly enhanced the selectivity efficiency of halide ions removal from sulfate solutions.

The enhanced selectivity is influenced by ion characteristics, electrostatic hindrances, dielectric effects, and membrane channel sizes, all stemming from differences in ion charges, sizes, and hydration energies. The selection of membrane preparation techniques plays a crucial role in achieving the desired selectivity, with methods like LbL assembly and electro-deposition methods enhancing selective separation. However, these methods tend to increase surface resistance and instability, requiring techniques such as electric-pulse deposition and chemical modifications to ensure prolonged stability. Fine-tuning AEM matrices through adjustments in alkyl spacer length and the incorporation of inorganic particles can also enhance halide ion selectivity. Moreover, precise control of operational conditions, such as current density, flow rate, pH, and stack design is essential to improve ion selectivity.

AEMs have demonstrated their effectiveness in removing halide ions from various industrial sulfate-based sources, such as brines from chemical industry processes, and spent zinc sulfate electrolyte within hydrometallurgical streams. These findings are valuable for addressing water quality concerns, resource management, and achieving cost-effective purification through the targeted elimination of undesired ions from different solution types. However, it is important to acknowledge that the specific outcomes of real-world implementations may exhibit variation due to factors like the composition of sulfate solutions, concentration of halide ions, design of the electro dialysis system, and intended application.

All in all, the use of AEMs in electro dialysis provide a selective and eco-friendly solution to tackle halide ion contamination, contributing to improved water quality and sustainable industrial operations. Their implementation holds the potential to safeguard both natural ecosystems and the performance of industrial processes, promoting a more environmentally conscious approach to halide ions removal in sulfate-rich wastewater.

CRedit authorship contribution statement

Önder Tekinalp: Conceptualization, Writing – original draft, Visualization. **Pauline Zimmermann:** Writing – review & editing. **Odne Stokke Burheim:** Supervision, Writing – review & editing. **Liyuan Deng:** Conceptualization, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The authors acknowledge the financial support from the Research Council of Norway (RCN-BIA) through the PRICE project (No. 294543).

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