

Contents lists available at ScienceDirect

Chemical Engineering Journal



journal homepage: www.elsevier.com/locate/cej

Optimizing microstructure of polyelectrolyte ion exchange membrane for electrodialysis

Jin Cheng^{a,1}, Weiyu Zhou^{b,1}, Meifeng Zhu^b, Zekai Zhang^a, Yijie Lu^b, Yakun Chen^b, Hongchun Mu^{a,*}, Cheng Lian^{a,*}, Honglai Liu^a

^a State Key Laboratory of Chemical Engineering, Shanghai Engineering Research Center of Hierarchical Nanomaterials, Frontiers Science Center for Materiobiology and Dynamic Chemistry, and School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237, China ^b International Elite Engineering School, East China University of Science and Technology, Shanghai 200237, China

ARTICLE INFO

Keywords: Polyelectrolyte multilayer membranes Ion exchange membrane Electrodialysis Poisson-Nernst-Planck equations Ion interception

ABSTRACT

In electrodialysis process, polyelectrolyte multilayer membranes (PEMMs) are introduced as a novel ion exchange membrane (IEM), as they can adjust different membrane structures according to the requirement. However, due to the influence of membrane structure on ion permeability and its mechanism have not been deeply studied, it is difficult to select the optimal structure under service conditions, resulting in low separation efficiency or increased energy consumption. Herein, a theoretical method is proposed to establish the structure-activity relationship of PEMMs, and then select the optimal membrane structure. The fixed charge was described by a specific trigonometric function to simulate the PEMMs. The effects of different membrane structures and charges on ion permeability and flux were studied by the modified Poisson-Nernst-Planck (MPNP) equations, and the competitive control relationship between the bilayers number and the charge density of each layer on the membrane performance was found. With our theoretical model, the selectivity and efficiency of PEMMs in electrodialysis can be comprehensively evaluated to guide its design and application.

1. Introduction

Electrodialysis is a traditional technology that uses the selective permeability of semi-permeable membrane to separate different solute ions [1,2]. It is developed for seawater desalination [3–5]. In the longterm development, new materials, membranes and technologies are gradually added to it. Now it is widely used in the chemical industry [6,7], light industry [8], metallurgy [9,10], papermaking [11,12] and pharmaceutical industry [13]. The core component of the electrodialysis process is the ion exchange membrane (IEM) [14]. It limits the passing ability of positively or negatively charged ions and is used to remove ions from water. IEM is mainly divided into anion exchange membrane and cation exchange membrane. Its essence is ion exchange resin, including polymer skeleton and fixed ions. However, due to the limitation of structure and process, the traditional IEM has the disadvantages of low component transfer flux, low selectivity, difficulty in flexible adjustment and high cost [15,16]. These limits the development of electrodialysis. Therefore, many scholars have introduced

polyelectrolyte multilayer membranes (PEMMs) into electrodialysis field as anion and cation exchange membranes [17,18]. Recently, some scholars have used the layer-by-layer polyelectrolyte functionalization approach to achieve the multicomponent separation of organic acids in a redox-flow electrodialysis platform, which can precisely tune the selectivity of organic acids [19]. Fig. 1b shows a more realistic microstructure of PEMMs, the polycations and polyanions were adsorbed alternately on the porous supporting membrane by layer-by-layer method [20,21]. The ion selectivity can be more easily controlled and optimized by adjusting the layer properties and adsorption conditions [22,23]. PEMMs are heterogeneous membranes, the charges cannot be evenly distributed layer-by-layer, so there will be an interlayer infiltration (interlacing) phenomenon. The great flexibility of PEMMs in structure and preparation can achieve specific selectivity and application. Since the above advantages, PEMMs have become a novel hot material in electrodialysis field. However, due to the influence of membrane structure on ion interception and its mechanism have not been deeply studied, it is difficult to choose the optimal membrane

* Corresponding authors.

¹ These authors contributed equally.

https://doi.org/10.1016/j.cej.2023.143669 Received 17 January 2023; Received in revised form 13 May 2023; Accepted 18 May 2023

Available online 23 May 2023 1385-8947/© 2023 Elsevier B.V. All rights reserved.

E-mail addresses: hongchunmu@ecust.edu.cn (H. Mu), liancheng@ecust.edu.cn (C. Lian).

structure under service conditions, resulting in low separation efficiency or increased energy consumption [24,25]. This has been a major pain point in electrodialysis field at present.

Previously, many researchers have made contributions to the research of IEMs to improve the separation performance of electrodialysis. Most of them focused on experiments and explored the relationship between structure and performance [26–28]. Many scholars have studied the transport process of salt through PEMMs through experiments, and reported the influence of the top layer, coating conditions and the increase of the increasing number of bilayers on the separation performance [29–32]. It is found that the concentration and sign of fixed charge in IEM are very important for the transport of mobile ions in the



Fig. 1. Schematic diagram of (a) electrodialysis process and (b) a set of electrodialysis chambers. The PEMMs prepared by alternating deposition layer by layer is mathematically treated as a specific trigonometric function $\sigma_{fix}(x) = g \cdot \sin(b\pi x) + r$. (c) A coarse-grained one-dimensional model of electrodialysis cell and its boundary conditions.

membrane. However, due to different industrial application purposes and use conditions, the evaluation criteria of the membrane are also very different, which makes it difficult to predict the separation effect and efficiency of the membrane.

According to the current situation of the field, rapid screening of the optimal polyelectrolyte membrane for different applications has become a thorny problem [33]. It can be seen that in essence, a theoretical prediction model is needed to quantitatively reveal the relationship between polyelectrolyte membrane and electrodialysis effect, so as to guide the use of membrane in electrodialysis. Previously, many researchers also focused on the modeling of IEM structure. Most of them use square wave charge model (fixed charges) to simulate the existence of IEMs, and use an approximation of the Poisson-Nernst-Planck (PNP) and the Navier-Stokes (NS) equations to study the transport through a nanochannel [34–36]. These works promote the scientific application of membrane in electrodialysis. However, most theoretical studies do not connect theory with practical systems, which has very limited guiding significance for industry. To sum up, our work aims to establish the structure-activity relationship between membrane structure and electrodialysis through a model and guide how to quickly find the optimal membrane.

In this work, the influence of different polyelectrolyte membrane structures on electrodialysis performance and efficiency was studied based on the modified PNP (MPNP) equations, which have been proved as an efficient approach to describe the dynamic process of charged ions in an electric field environment [37-39]. This method has been introduced into the study of polyelectrolyte or layer-by-layer membranes and has shown considerable accuracy [40-43]. We propose a new model, which uses the fixed charge in the form of a trigonometric function to simulate the PEMMs with alternating cation and anion layers. This setting is more realistic than the previous square wave charge model (Section 2.2 for details). The MPNP equations also consider the size of ions, which is more accurate than PNP equations in dealing with electric double layer structure and actual ion model [44-47]. The optimal membrane structure can be found by adjusting the concentration of fixed charges, the bilayers number within the unit width, and the net charge carried by the membrane. The influence of membrane structure on ion flux is also studied. The framework of this work is as follows. Firstly, the trigonometric function model and research system of PEMMs are described, and the MPNP method used in this work is briefly introduced. Next, we discuss the effects of different membrane structures and charge distributions on ion permeability and ion flux, and make suggestions on the structural design of IEM. Finally, the main results and possible implications for the future are summarized.

2. Molecular model and theory

2.1. Model description

As shown in Fig. 1a, a complete electrodialysis process includes many identical electrodialysis chambers for layer-by-layer filtration, which are separated by electrodialysis membranes. Anion and cation exchange membranes are used alternately to create ion rich and ion depleted channels. The same principle applies to electrodialysis using PEMMs. PEMMs can be flexibly manufactured as anion and cation exchange membranes by adding any positive or negative charges. It can adapt to different electrodialysis conditions. In order to explore the influence of membrane structure on electrodialysis effect, we only need to model a set of electrodialysis chamber (Fig. 1b). Similar to previous studies [44,47], we have established a coarse-grained one-dimensional model, with a certain thickness of membrane in the middle, which is surrounded by two free electrolyte domains with the same length. We simulated the transport of three ions (A^+ , B^- and C^-), and added fixed charges to the intermediate IEM domain in the form of sine function. For this experimental system, the cation exchange membrane is simulated. A scenario of ion removal is simulated, similar to seawater desalination.

The direction of the electric field is to the left, so the anion moves to the right, and the cation exchange membrane will block it. Cations move to the left and can freely pass through the cation exchange membrane. The left side will form an ion rich chamber, and the right side will be an ion depleted chamber. A^+ ion can pass through freely, while B^- ion is blocked. On the leftmost and rightmost outer boundaries, because it is connected with the outside world, turbulence can ensure good mixing effect, so it can be considered that the concentration outside the diffusion boundary layer on both sides of the membrane is constant.

2.2. Mathematical treatment of PEMMs

In the model, the space charges need to be divided into moving ions and fixed ions, in which the fixed ions are the composition of the membrane. As shown in Fig. 2a, in the previous simulation work [48,49], most IEM assumed that the ion concentration is fixed (constant) and the adsorbed ions are arranged orderly. Therefore, square wave charge function is used to describe IEM, which is very unsatisfactory and inaccurate. Although this model has also been used in some studies, it is too idealistic and divorced from the actual situation. Some scholars have previously discovered the ionic crosslinking effect, known as intrinsic compensation [50,51], as shown in Fig. 2b. Considering this phenomenon, we creatively propose to describe PEMMs in the form of sine function, which is in good agreement with the structure of alternating cation and anion multi-layers [34,48,49]. Therefore, our model can more accurately simulate the IEM structure based on keeping simplicity. As shown in Fig. 1b&2, our simplified fixed ion form is as follows:

$$\sigma_{fix}(x) = g \cdot \sin(b\pi x) + r \tag{1}$$

The model can also adjust the charge on the membrane. Where g is the amplitude of the charge density of each layer (the charge of each adsorption layer), b is used to control the bilayers number within the unit width, that is, the arrangement tightness, r determines the vertical shift of the function and can adjust the net charge density of the membrane. Fig. 2b shows the physical meaning of the parameters g, b, r on the model function. Electrodialysis usually uses alternating anion and cation membranes to control the ion permeability, which is equivalent to the positive and negative adjustment of parameter r. Although different processes and conditions will affect the specific morphology of the membrane, it is reasonable to regard it as a sine function within the range of actual membrane thickness.

2.3. Governing equations and chemical potential

In order to describe the dynamic process of electrodialysis, we need to establish the continuity and diffusion equations.

$$\frac{\partial \rho_i}{\partial t} = -\nabla \cdot J_i + R_i \tag{2}$$

$$J_i = -\frac{D_i}{k_B T} \rho_i \nabla \mu_i \tag{3}$$

where ρ_i represents the local number density of specie *i*, J_i stands for the mass flux, μ_i stands for the local electrochemical potential, k_B is the Boltzmann constant, *T* is the absolute temperature, D_i is the diffusion constant. The R_i is the source term, representing the unsteady term that cannot be included in the governing equation.

According to the basic principle of MPNP equations, the intrinsic chemical potential is obtained by minimizing the grand potential, as described in SI. It can be seen from the derivation that the MPNP equation additionally considers the size effect of matter based on PNP equation, so it has higher accuracy. However, in order to balance accuracy and calculation speed, MPNP does not consider more subtle interactions, such as direct Coulombic energy, electrical correlations, etc. At the mesoscopic scale, the impact of these interactions is very small. The chemical potential of each ionic species is



(a) Ideal membrane structure (b) Actual polyelectrolyte deposition

Fig. 2. Compared with the traditional model, the new model is more in line with the actual situation. The physical meaning of membrane structure parameters *g*, *b*, *r* is marked.

$$\mu_i = \pm e\psi + k_B T \left[\ln\left(a^3 \rho_i\right) - \ln\left(1 - \sum_i a^3 \rho_i\right) \right]$$
(4)

where *e* represents the unit charge, *a* stands for the diameter of hard spheres, and ψ stands for the local electrical potential. The potential of each point of the system can be accurately solved by Poisson equation:

$$\nabla^2 \psi = -\frac{e}{\varepsilon_r \varepsilon_0} \left(\sum_i z_i \rho_i + \rho_{fix} \right)$$
(5)

where ε_r the relative permittivity, $\varepsilon_0 = 8.854 \times 10^{-12}$ F/m is the absolute dielectric constant, z_i the valence of specie *i*. Then, we substitute equation (4) into (3) to obtain

$$J_{i} = -D\left[\pm\rho_{i}\frac{e}{k_{B}T}\nabla\psi + \nabla\rho_{i} + \frac{a^{3}\rho_{i}}{1 - \sum_{i}a^{3}\rho_{i}}\nabla\left(\sum_{i}\rho_{i}\right)\right]$$
(6)

Substitute Eq. (6) into (2) to get the complete continuity equation. In summary, the MPNP equation applicable to the electrodialysis system is:

$$\nabla^{2} \psi = -\frac{e}{\varepsilon_{r} \varepsilon_{0}} \left(\sum_{i} z_{i} \rho_{i} + \rho_{fix} \right)$$

$$\rho_{fix}(x) = g \cdot \sin(b\pi x) + r$$

$$\frac{\partial \rho_{\pm}}{\partial t} = D \left(\nabla^{2} \rho_{\pm} \pm \frac{e}{k_{B}T} \nabla \cdot (\rho_{\pm} \nabla \psi) + \nabla \cdot \left[\frac{a^{3} \rho_{\pm}}{1 - a^{3} \rho_{+} - a^{3} \rho_{-}} \nabla (\rho_{+} + \rho_{-}) \right] \right)$$
(7)

In order to simplify the calculation, the equation is dimensionless.

We turn the continuity equations into the following equations and solve them simultaneously:

$$\frac{\partial^2 \phi}{\partial x^{*2}} = -\frac{1}{2\zeta^2} \left(\rho_+^* - \rho_-^* + \rho_{fix}^* \right)$$
$$\rho_{fix}^* (x^*) = \frac{g \cdot \sin(b\pi x^*) + r}{\rho_s}$$
$$\frac{\partial \rho_{\pm}^*}{\partial t^*} = \zeta \left(\frac{\partial^2 \rho_{\pm}^*}{\partial x^{*2}} \pm \frac{\partial}{\partial x^*} \left(\rho_{\pm}^* \frac{\partial \phi}{\partial x^*} \right) + \frac{\partial}{\partial x^*} \left[\frac{\eta \rho_{\pm}^*}{1 - \eta \left(\rho_+^* + \rho_-^* \right)} \frac{\partial}{\partial x^*} \left(\rho_+^* + \rho_-^* \right) \right] \right)$$
(8)

where $x^* = x/L$, $\phi = (e\psi)/(k_BT)$, $\rho_i^*(i = +, -, fix) = \rho_i/\rho_s$ with ρ_s being the bulk number density of cations or anions, $t^* = t/\tau_{RC}$ with $\tau_{RC} = \lambda_D L/D$, $\lambda_D = \sqrt{\varepsilon_0 \varepsilon_r k_B T/2e^2 \rho_s}$ is the Debye screening length, $\eta = a^3 \rho_s$. In order to facilitate the control and discussion of simulation, we introduce a dimensionless scaling factor, $\zeta = \lambda_D/L$. Therefore, for the dimensionless variables in the equations, their numerical results are controlled by only two basic parameters, i.e., η and ζ . In physical sense, regulating these two parameters is to adjust the ionic density ρ_s and the system size L.

2.4. Parameter setting and boundary conditions

When describing electrodialysis dynamics, MPNP equation needs three kinds of parameters related to system characteristics, boundary conditions and initial values. For this work, for the simplicity and universality of the model, considering the diameter of general hydrated ions, the ionic system is defined by particle size a = 0.5 nm, valence $|z_i| = 1$, a single diffusivity for all particles $D = 2 \times 10^{-9}$ m²/s. In this work, whenever the ionic species are explicitly considered, the relative dielectric constant is adopted $\varepsilon_r = 78$ to explain the dispersion interaction and ionic polarizability of the aqueous solution not included in the coarse particle model. The same diffusion coefficient is used in the membrane and solution. The set ions have no other difference except the valence. The main influence of diffusion coefficient on the system is the ion diffusion rate. Our result analysis is based on the result that the system relaxation is stable. Therefore, the uniform setting of dielectric constant and ion diffusion coefficient will not affect the law of the membrane structure on ion permeability [52,53]. System temperature T = 293.15 K, and simulated dialysis chamber width $L = 100 \lambda_D$. We have $\lambda_D \approx 1$ nm, $L \approx 100$ nm.

When studying the dynamics of electrodialysis, we assume that the

bias potential $\phi_0 = 10$ is initially applied to two electrodes (at t = 0). According to the one-dimensional model shown in Fig. 1c, the boundary conditions of the electric field are as follows:

$$\phi(+L,t>0) = \phi_0
\phi(-L,t>0) = 0$$
(9)

Due to we consider a stable electrodialysis process, we need to set the ion concentration at different boundaries to make them flow at a certain ion concentration field.



Fig. 3. (a) Under g = 1 and r = 0, the potential distribution of different *b*, which represents that the highest charge concentration of each layer is 0.1 M and the net charge of the whole membrane is 0. (b) Enlarge the part of the membrane. (c) When b = 36 and r = 0, the potential distribution of different layer charges. (d) When g = 5 and b = 36, the potential distribution changes with the net charge of the whole membrane. (e) The compact alternation of cation and anion leads to serious ionic interlacing, shielding a certain potential. (f) Schematic diagram of membrane potential change.

$$\rho_{A}(\pm L, t) = 0.1 \text{ M}$$

$$\rho_{B}(-L, t) = 0.1 \text{ M}$$

$$\rho_{C}(+L, t) = 0.1 \text{ M}$$

$$\frac{\partial \rho_{i}(i = +, -)}{\partial x}(\pm L, t) = 0$$
(10)

The MPNP equations can describe the dynamic relaxation process of ionic density distributions under electric field until a new equilibrium is established in the system. The time range we simulated is from 0 to 500 τ_{RC} with $\tau_{RC} = \lambda_D L/D$.

According to the research scheme of the variable-controlling approach, the amount of charge on each layer g = 1 (charge density 0.1 mol/L) and the net charge density r = 0 are fixed first, and the bilayers number within the unit width *b* is explored. For electrodialysis, the IEM with charge density less than 1 mol/L is generally used. More concentrations (0.1 \sim 0.9 mol/L) are also explored later. After determining the optimal *b*, r = 0 is still fixed to explore the impact of *g*. Finally, fix *b* and *g* to explore the effect of *r*. The optimal membrane

structure is explored in a step-by-step manner.

3. Results and discussion

3.1. Serrated potential distribution in membrane

According to MPNP equations, the potential distribution under different membrane conditions can be obtained directly. The electric field, as the driving force of ion transport, determines the ion distribution of the chamber, which is the basic factor for the study of membrane structure and ion permeability. Since the influence of membrane structure on electric field and ion distribution is the fundamental reason for ion transport and permeability, this is the starting point for analysis.

It can be seen from Fig. 3 that the membrane structure directly determines the potential distribution. We adjust the bilayers number within the unit width, the charge of each layer and the overall electricity, and observe the potential distribution. In Fig. 3a&b, more dense membrane layers (more bilayers per unit length) will lead to more



Fig. 4. (a) Three ion distributions at g = 1, r = 0 and b = 36. (b) Enlarge the part of the membrane. The *B*' ion distribution under different *b* when (c) g = 1, r = 0, (d) b = 36, r = 0 and (e) g = 1, r = 1. (f) When b = 36 and g = 5, the *B*' ion distribution under different *r*. The net charge on the membrane is one of the determinants of the interception effect.

oscillation cycles of the potential, but the extreme value of the potential will decrease, which is because the dense alternating structure of cation and anion leads to serious ion interlacing (Fig. 3e). This makes the charges on each layer shield each other to some extent. In addition, higher g means higher layer charge, which will lead to higher interlayer potential difference (Fig. 3c). As shown in Fig. 3d, if we adjust the net charge on the membrane (*r*), it will lead to the overall change of the membrane potential. Fig. 3f shows the schematic diagram of the potential changing with different membrane parameters. The alternating layer-by-layer membrane structure leads to serrated potential distribution, which will directly determine the selective passage of ions, and provide a theoretical basis for the experimental results.

3.2. Ion distribution trapped by the membrane

The changing potential leads to different ion distribution, which in turn affects the potential. After the system begins to relax, the potential and ions reach equilibrium in the interaction. As shown in Fig. 4**a**&**b**, A^+ and B^- are alternately distributed in the membrane, regardless of the membrane charge, the direction of the electric field will drive A^+ to transfer to the left. The boundary conditions of B^- and C^- concentrations determine the overall flux direction of these ions. The direction of the electric field explains why B⁻ transmits to the right at a faster rate and C⁻ transmits to the left at a slower rate. As previously mentioned, this membrane is a cation exchange membrane. A^+ can pass through freely, while B^{-} is blocked. In this way, ion rich and ion depleted channels can be obtained. The A^+ concentration on both membrane sides is basically the same, so the permeability of B^- is selected to describe the membrane ion selectivity. Fig. 4c-f shows the distribution of B^- under various conditions. According to Fig. 4c-f, each polyelectrolyte layer will intercept some ions, so the B^- concentration on the left is higher than right. Theoretically, more bilayers will bring better selectivity, but the compact bilayers lead to the reduction of moving ion concentration on each layer, which is due to the charge shielding caused by ion interlacing (Fig. 4c). This also leads to the competitive control relationship between the bilayers number within the unit width and the charge density of each layer on the membrane permeability. Therefore, there will be an optimal bilayers number within the unit width. Furthermore, increasing the charge density of each layer is also a solution to improve the interception rate (Fig. 4d). As can be seen from Fig. 4e&f, the potential shows a controlling effect on the ion distribution, and the change of membrane net charge will lead to great differences in the ion distribution, which is one of the decisive factors of the interception effect.

3.3. Effect of membrane structure on ion permeability

Based on obtaining the ion distribution, we need to quantitatively describe the effect of different membrane structures on ion selective permeability. As described in Section 2.1, this is a scenario of ion removal. Cations can move freely to the left. The anion moves to the right, and the cation exchange membrane will block it. For this cation exchange membrane, it is necessary to explore its blocking effect on anions. Therefore, the permeability of B^- is selected to describe the membrane ion selective permeability, which is more representative and helps to draw conclusions. After obtaining the ionic concentrations value of each x-coordinate in the known domain, the ion interception effect of the membrane can be calculated using the following formula [54]:

$$R_i = 1 - \frac{c_{i,p}}{c_{i,f}} \tag{11}$$

where $c_{i,p}$ and $c_{i,f}$ is the concentration of *i* ions on the membrane permeate (right) and feed (left) side, respectively, which is selected as the concentration close to the surface on both sides of the membrane. The system potential only determines the overall driving force, and will

not affect the general law of interception effect under the same potential. Therefore, it is only necessary to explore the structure–activity relationship at one potential ϕ_0 .

Firstly, according to the needs of the simulation scene, the permeability of B^- is selected to describe the membrane ion selectivity. The influence of the bilayers number on the ion repulsion rate under various membrane charges is studied. A higher R value means that the cation exchange membrane has better blocking effect on anions. It can be found that b = 36 has the best ion selectivity (Fig. 5a-d). The reason can be obtained from the potential distribution and ion distribution. More bilayers per unit width (larger b value) results in more frequent potential alternations and lower potential extremes. For ion interception rate, more bilayers will bring better selectivity, but the reduced potential extreme value will worsen the results. Therefore, when changing b, these two factors compete to determine the ion interception rate (Fig. 5e). When *b* less than 36, the bilayers number is the dominant factor (Fig. 5e upper part). However, when b > 36, the extreme value change of potential in each layer becomes the dominant factor (Fig. 5e lower part). Based on this, we can determine the optimal number of bilayers. Since the PEMMs is adsorbed on the substrate layer-by-layer, the parameter b can be adjusted by controlling the thickness of each layer. In addition, some scholars have also studied the dependence of ion permselectivity on the layers number in experiment [55]. Similar to the results obtained in Fig. 5, the corresponding curves have the same trend of change.

After obtaining the optimal number of bilayers, the result b = 36 can be used to explore the influence of each layer charge density g on the interception rate. As shown in Fig. 6a&b, set b = 36 and r = 0, the increase of charge will lead to a larger potential difference, which will bring stronger repulsion and increases the ion interception concentration of each layer. Therefore, larger g leads to better interception rate.

To sum up, the optimal membrane structure can be determined, including the bilayers number within the unit width and layer charge density. On this basis, the effect of net charge r on the interception was evaluated (Fig. **6c&d**). Adding a negative charge to the membrane will greatly reduce the permeability of anions and improve the interception rate, but it will soon reach stability at the charge density of 0.2 mol/L.

3.4. Effect of membrane structure on ion transport efficiency

The structure difference of IEM will lead to different separation properties and seriously affect the resistance of ion permeation, which means that the ion flux will be different under the same concentration difference and electric field driving force. Therefore, it is necessary to study the ion flux under different conditions, which will have important guiding significance for the energy consumption under working conditions. Due to the use of solution diffusion coefficient for the entire system, the flux value may be slightly higher, but it does not affect the flux variation pattern. We find that the flux decreases first and then increases with *b* except g = 1, and the flux is the smallest when b = 20 (Fig. 7a&b). This is because more layers will increase the ion transmission resistance, but the increase of membrane layers means the decrease of layer fixed charge density, which will reduce the ion transmission resistance. There is a competitive control relationship between them on ion flux. Fig. 7c shows the relationship between ion flux and membrane net fixed charge concentration. Select parameter r from 0 to 10 (net charge of membrane 0 \sim 1 mol/L). Higher charge density means greater resistance. In addition, we also found that some scholars have tested the ion fluxes through the studied membrane during the electrodialysis process [56], which is similar to the research results in Fig. 7a&b. As the layers number increases, the flux first decreases and then increases, and there is a lowest point.

In addition, according to the following formula, the current efficiency was calculated, which reflects the energy utilization of the ion removal.



Fig. 5. (a) When g = 1, (b) g = 3, (c) g = 5, (d) g = 9, B^{-} ion interception rate under different *b*. The bilayers number within the unit width b = 36 is the best in all cases. (e) Schematic diagram of membrane selective permeability under different ion cycles.

$$\eta = \frac{3600(c_{i,f} - c_{i,p})VF}{It} \times 100\%$$
(12)

where *V* is the volume of effluent from the dialysis chamber, m^3 , *F* is the Faraday constant, 96,485C·mol⁻¹, *I* is the operating current, *A*, *t* is the time, *s*. As shown in Fig. 7d, higher *g* leads to better separation, and therefore higher current efficiency, which means that energy utilization

is more efficient. At the same g, the current efficiency is also highest around b = 36. Considering energy consumption, membranes with higher current efficiency should be selected.

3.5. Optimization of microstructure of PEMMs

Through the above results, the effects of various factors on mem-



Fig. 6. (a) The effect of charge density of each layer of ions in the membrane on ion interception. (b) Schematic diagram of how different *g* affect ion interception. (c) The effect of net charge density of PEMMs on ion interception. (d) Schematic diagram of how different *r* (net charge density) affect ion interception.



Fig. 7. When g = 1, 3, 5 and 9, B^r ion (a) dimensionless flux and (b) flux under different *b*. Except for g = 1, the flux decreases first and then increases. When b = 20, the flux is the smallest. (c) When g = 5, b = 36, B^r ion flux under different *r*. (d) When g = 1, 3, 5 and 9, current efficiency under different *b*.

brane properties can be summarized, and then the required membrane structure can be designed. Due to the dimensionless treatment of our model, parameter of the bilayers number in membrane b = 36 brings the best ion interception rate under the common ion size a = 0.5 nm, because it balances the arrangement density of fixed ions and the charge density of each layer. If the ion size is fixed, this parameter is fixed in the dimensionless model. Owing to $x^* = x/L$, the thickness of each bilayer in the membrane is

$$l_{+-}(b=36) = \frac{2L}{b} = \frac{L}{18}$$
(13)

Since L = 100 nm, this means that the thickness of each bilayer is about 5.55 nm. The thickness of each layer of anions or cations is half of l_{+-} , which is L/b. It can be adjusted by controlling the thickness of each adsorption layer in PEMMs. In this work, the most common situation is set, but the optimal bilayers number varies depending on the size and charge of the ions. Therefore, in order to obtain the optimal bilayers number under actual working conditions, it is necessary to set parameters (including ion size, valence, concentration, membrane thickness, etc.) based on actual usage conditions, and then use the above model to simulate to find the optimal bilayers number. If our optimization goal is to maximize the interception rate, we also need to improve each layer charge density g and net charge density r as much as possible. A larger parameter g will improve the interception rate of each layer, which can be achieved by doping more ions into the polyelectrolyte. And the net charge density r can be achieved by branching ions on the membrane.

Higher interception generally leads to higher membrane resistance, the ion flux will be greatly reduced. In this usage scenario, it is necessary to reduce the transport of B^{-} ions (*b* approaching 20) and increase the net charge density *r*. In addition, considering the impact of current efficiency, *b* should be between 20 and 36. For important applications of electrodialysis (including seawater desalination), the main target ions are metal ions, such as sodium and potassium ions. Their hydration diameter is approximately 0.6 nm, which is close to the diameter set in this work. The main conclusions of this work are applicable to seawater desalination systems. However, there may be subtle differences in values (specific *b* or *g* values). The specific membrane structure should be set according to the corresponding working conditions, and then the conclusions can be drawn through simulation. The performance focus of the PEMMs should match the applying purposes.

4. Summary and conclusions

In summary, a new fixed charge model in trigonometric function form is proposed to simulate the IEM, and the dynamic process is simulated by MPNP equations. The ion interception rate and flux are obtained, and the influence of IEM structure on ion permeability is explored. The main conclusions are as follows.

- 1. The membrane structure affects the ion density distribution by affecting the potential distribution, which is the fundamental reason for affecting the membrane performance.
- 2. It is discovered that the bilayers number within the unit width and the charge density of each layer have a competitive control relationship over the ion permeability. The compact alternation of cation and anion leads to serious ion interlacing, shielding a certain potential, and then reducing the interception rate.
- 3. The flux decreases first and then increases with the bilayers number, with a minimum value. Higher net charge density of the membrane brings greater resistance (smaller flux), which means higher energy consumption.
- 4. According to the model, the ion selectivity and efficiency of different membranes were evaluated, and guiding opinions were put forward for screening the optimal structure according to the applying purposes. The membrane structure can be regulated by the thickness of

the adsorption layer, the addition of ions, and the branching of specific charged ions.

Importantly, this model can be used to describe any polyelectrolyte membrane separation system. We believe that this work has a certain guiding significance for the industrial application of membrane separation, and hope that it will stimulate future research of membrane separation industry.

CRediT authorship contribution statement

Jin Cheng: Investigation, Methodology, Formal analysis, Visualization, Writing – original draft. Weiyu Zhou: Software, Formal analysis, Visualization, Writing – original draft. Meifeng Zhu: Software, Formal analysis. Zekai Zhang: Writing – review & editing. Yijie Lu: Formal analysis. Yakun Chen: Formal analysis. Hongchun Mu: . Cheng Lian: . Honglai Liu: Resources.

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

This work was sponsored by the National Key R&D Program of China (No. 2021YFB3801301), the State Key Laboratory of Clean Energy Utilization (Open Fund Project No. ZJUCEU2021005), the Fundamental Research Funds for the Central Universities (2022ZFJH004), the National Natural Science Foundation of China (No. 22278127) and the Shanghai Rising-Star Program (No. 21QA1401900). Cheng Jin thanks Ms. Zhang Man for her helpful discussion.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2023.143669.

References

- S. Al-Amshawee, M.Y.B.M. Yunus, A.A.M. Azoddein, D.G. Hassell, I.H. Dakhil, H. A. Hasan, Electrodialysis desalination for water and wastewater: A review, Chem. Eng. J. 380 (2020) 122231.
- [2] A.A. Uliana, N.T. Bui, J. Kamcev, M.K. Taylor, J.J. Urban, J.R. Long, Ion-capture electrodialysis using multifunctional adsorptive membranes, Science 372 (6539) (2021) 296–299.
- [3] A.S. Behrman, Electroosmotic water purification, J. Chem. Educ. 6 (10) (1929) 1611.
- [4] L. Gurreri, A. Tamburini, A. Cipollina, G. Micale, Electrodialysis Applications in Wastewater Treatment for Environmental Protection and Resources Recovery: A Systematic Review on Progress and Perspectives, Membranes 10 (7) (2020) 146.
- [5] A. Campione, L. Gurreri, M. Ciofalo, G. Micale, A. Tamburini, A. Cipollina, Electrodialysis for water desalination: A critical assessment of recent developments on process fundamentals, models and applications, Desalination 434 (2018) 121-160.
- [6] O.M.K. Readi, M. Gironès, W. Wiratha, K. Nijmeijer, On the isolation of single basic amino acids with electrodialysis for the production of biobased chemicals, Ind. Eng. Chem. Res. 52 (3) (2013) 1069–1078.
- [7] Y. Mei, L. Liu, Y.-C. Lu, C.Y. Tang, Reverse Electrodialysis chemical cell for energy harvesting from controlled acid-base neutralization, Environ. Sci. Tech. 53 (8) (2019) 4640–4647.
- [8] J.-X. Zhuang, Q. Chen, S. Wang, W.-M. Zhang, W.-G. Song, L.-J. Wan, K.-S. Ma, C.-N. Zhang, Zero discharge process for foil industry waste acid reclamation: Coupling of diffusion dialysis and electrodialysis with bipolar membranes, J. Membr. Sci. 432 (2013) 90–96.
- [9] K.L. Timofeev, A.B. Lebed, A.J. Malyutin, Deep treatment of copper plant waste water streams with water recycling, Solid State Phenom. 265 (2017) 937–944.

J. Cheng et al.

- [10] M. Regel-Rosocka, A review on methods of regeneration of spent pickling solutions from steel processing, J. Hazard. Mater. 177 (1–3) (2010) 57–69.
- [11] Z. Zhang, S. Ge, C. Jiang, Y. Zhao, Y. Wang, Improving the smoking quality of papermaking tobacco sheet extract by using electrodialysis, Membr. Water Treatment 5 (1) (2014) 31–40.
- [12] C.R. Li, S.L. Ge, W. Li, et al., Desalting of papermaking tobacco sheet extract using selective electrodialysis, Membr. Water Treatment 8 (4) (2017) 381–393.
- [13] A.A. Konarev, Use of electrodialysis in the pilot- and commercial-scale production of pharmaceutical substances, Russ. J. Electrochem. 51 (12) (2015) 1124–1134.
- [14] M.A.C.K. Hansima, M. Makehelwala, K.B.S.N. Jinadasa, Y. Wei, K.G. N. Nanayakkara, A.C. Herath, R. Weerasooriya, Fouling of ion exchange membranes used in the electrodialysis reversal advanced water treatment: A review, Chemosphere 263 (2021) 127951.
- [15] Y. Zhu, M. Ahmad, L. Yang, M. Misovich, A. Yaroshchuk, M.L. Bruening, Adsorption of polyelectrolyte multilayers imparts high monovalent/divalent cation selectivity to aliphatic polyamide cation-exchange membranes, J. Membr. Sci. 537 (2017) 177–185.
- [16] J. Jang, Y. Kang, K. Kim, S. Kim, M. Son, S.-S. Chee, I.S. Kim, Concrete-structured Nafion@MXene/Cellulose acetate cation exchange membrane for reverse electrodialysis, J. Membr. Sci. 646 (2022) 120239.
- [17] N. White, M. Misovich, A. Yaroshchuk, M.L. Bruening, Coating of nafion membranes with polyelectrolyte multilayers to achieve high monovalent/divalent cation electrodialysis selectivities, ACS Appl. Mater. Interfaces 7 (12) (2015) 6620–6628.
- [18] N. White, M. Misovich, E. Alemayehu, A. Yaroshchuk, M.L. Bruening, Highly selective separations of multivalent and monovalent cations in electrodialysis through Nafion membranes coated with polyelectrolyte multilayers, Polymer 103 (2016) 478–485.
- [19] N. Kim, J. Lee, X. Su, Precision tuning of highly selective polyelectrolyte membranes for redox-mediated electrochemical separation of organic acids, Adv. Funct. Mater. 33 (12) (2023) 2211645.
- [20] J. de Grooth, B. Haakmeester, C. Wever, J. Potreck, W.M. de Vos, K. Nijmeijer, Long term physical and chemical stability of polyelectrolyte multilayer membranes, J. Membr. Sci. 489 (2015) 153–159.
- [21] S. Ilyas, R. English, P. Aimar, J.-F. Lahitte, W.M. de Vos, Preparation of multifunctional hollow fiber nanofiltration membranes by dynamic assembly of weak polyelectrolyte multilayers, Colloids Surf. A Physicochem. Eng. Asp. 533 (2017) 286–295.
- [22] S.-Y. Sun, X.-Y. Nie, J. Huang, J.-G. Yu, Molecular simulation of diffusion behavior of counterions within polyelectrolyte membranes used in electrodialysis, J. Membr. Sci. 595 (2020).
- [23] V. Titorova, K. Sabbatovskiy, V. Sarapulova, E. Kirichenko, V. Sobolev, K. Kirichenko, Characterization of MK-40 membrane modified by layers of cation exchange and anion exchange polyelectrolytes, Membranes 10 (2) (2020) 20.
- [24] D.W. Shin, M.D. Guiver, Y.M. Lee, Hydrocarbon-based polymer electrolyte membranes: importance of morphology on ion transport and membrane stability, Chem. Rev. 117 (6) (2017) 4759–4805.
- [25] C. Cheng, N. White, H. Shi, M. Robson, M.L. Bruening, Cation separations in electrodialysis through membranes coated with polyelectrolyte multilayers, Polymer 55 (6) (2014) 1397–1403.
- [26] J.R. Varcoe, P. Atanassov, D.R. Dekel, A.M. Herring, M.A. Hickner, P.A. Kohl, A. R. Kucernak, W.E. Mustain, K. Nijmeijer, K. Scott, T. Xu, L. Zhuang, Anion-exchange membranes in electrochemical energy systems, Energ. Environ. Sci. 7 (10) (2014) 3135–3191.
- [27] A. Ali, R.A. Tufa, F. Macedonio, E. Curcio, E. Drioli, Membrane technology in renewable-energy-driven desalination, Renew. Sustain. Energy Rev. 81 (2018) 1–21.
- [28] T. Luo, S. Abdu, M. Wessling, Selectivity of ion exchange membranes: A review, J. Membr. Sci. 555 (2018) 429–454.
- [29] L. Ouyang, R. Malaisamy, M.L. Bruening, Multilayer polyelectrolyte films as nanofiltration membranes for separating monovalent and divalent cations, J. Membr. Sci. 310 (1) (2008) 76–84.
- [30] J. de Grooth, R. Oborný, J. Potreck, K. Nijmeijer, W.M. de Vos, The role of ionic strength and odd–even effects on the properties of polyelectrolyte multilayer nanofiltration membranes, J. Membr. Sci. 475 (2015) 311–319.
- [31] A. Szymczyk, H. Zhu, B. Balannec, Ion Rejection properties of nanopores with bipolar fixed charge distributions, J. Phys. Chem. B 114 (31) (2010) 10143–10150.
- [32] H. Tao, G. Li, Z. Xu, C. Lian, H. Liu, Optimizing pore structure of nanoporous membranes for high-performance salinity gradient power conversion, Chem. Eng. J. 444 (2022) 136675.

- [33] J. Cheng, J. Xu, J. Yang, W. Lv, C. Lian, H. Liu, Enhanced oil recovery by sacrificing polyelectrolyte to reduce surfactant adsorption: A classical density functional theory study, Chem. Eng. Sci. 261 (2022) 117957.
- [34] E. Evdochenko, J. Kamp, R. Femmer, Y. Xu, V.V. Nikonenko, M. Wessling, Unraveling the effect of charge distribution in a polyelectrolyte multilayer nanofiltration membrane on its ion transport properties, J. Membr. Sci. 611 (2020) 118045.
- [35] A.V. Kovalenko, A.M. Uzdenova, M.K. Urtenov, et al., Criterion numbers of electroconvection in electrodialysis desalting compartment, Condensed Matter Interphases 15 (4) (2013) 404–412.
- [36] A. Gross, A. Morvezen, P. Castillo Gomez, X. Xu, P. Xu, Numerical investigation of the effect of two-dimensional surface waviness on the current density of ionselective membranes for electrodialysis, Water 11 (7) (2019) 1397.
- [**37**] H. Tao, G. Chen, C. Lian, H. Liu, M.-O. Coppens, Multiscale modeling of ion transport in porous electrodes, AIChE J. 68 (4) (2022) e17571.
- [38] C. Lian, M. Janssen, H. Liu, R. van Roij, Blessing and curse: how a supercapacitor's large capacitance causes its slow charging, Phys. Rev. Lett. 124 (7) (2020), 076001.
- [39] Y. Lin, C. Lian, M.U. Berrueta, H. Liu, R. van Roij, Microscopic model for cyclic voltammetry of porous electrodes, Phys. Rev. Lett. 128 (20) (2022), 206001.
- [40] H. Dartoomi, M. Khatibi, S.N. Ashrafizadeh, Enhanced ionic current rectification through innovative integration of polyelectrolyte bilayers and charged-wall smart nanochannels, Anal. Chem. 95 (2) (2023) 1522–1531.
- [41] M. van Soestbergen, P.M. Biesheuvel, R.T.H. Rongen, L.J. Ernst, G.Q. Zhang, Modified Poisson–Nernst–Planck theory for ion transport in polymeric electrolytes, J. Electrostat. 66 (11-12) (2008) 567–573.
- [42] P. Berg, B.E. Benjaminsen, Effects of finite-size ions and relative permittivity in a nanopore model of a polymer electrolyte membrane, Electrochim. Acta 120 (2014) 429–438.
- [43] R. Kodým, V. Fíla, D. Šnita, K. Bouzek, Poisson–Nernst–Planck model of multiple ion transport across an ion-selective membrane under conditions close to chloralkali electrolysis, J. Appl. Electrochem. 46 (6) (2016) 679–694.
- [44] J. Cheng, H. Tao, K.e. Ma, J. Yang, C. Lian, H. Liu, J. Wu, A theoretical model for the charging dynamics of associating ionic liquids, Front. Chem. Eng. 4 (2022), 852070.
- [45] H. Tao, C. Lian, H. Liu, Multiscale modeling of electrolytes in porous electrode: From equilibrium structure to non-equilibrium transport, Green Energy Environ. 5 (3) (2020) 303–321.
- [46] K. Ma, M. Janssen, C. Lian, R. van Roij, Dynamic density functional theory for the charging of electric double layer capacitors, J. Chem. Phys. 156 (8) (2022) 084101.
- [47] J. Yang, M. Janssen, C. Lian, R. van Roij, Simulating the charging of cylindrical electrolyte-filled pores with the modified Poisson–Nernst–Planck equations, J. Chem. Phys. 156 (21) (2022) 214105.
- [48] R.A. Ghostine, M.Z. Markarian, J.B. Schlenoff, Asymmetric growth in polyelectrolyte multilayers, J. Am. Chem. Soc. 135 (20) (2013) 7636–7646.
- [49] Y.I. Dirir, Y. Hanafi, A. Ghoufi, A. Szymczyk, Theoretical investigation of the ionic selectivity of polyelectrolyte multilayer membranes in nanofiltration, Langmuir 31 (1) (2015) 451–457.
- [50] M. Lösche, J. Schmitt, G. Decher, W.G. Bouwman, K. Kjaer, Detailed structure of molecularly thin polyelectrolyte multilayer films on solid substrates as revealed by neutron reflectometry, Macromolecules 31 (25) (1998) 8893–8906.
- [51] J.B. Schlenoff, S.T. Dubas, Mechanism of polyelectrolyte multilayer growth: charge overcompensation and distribution, Macromolecules 34 (3) (2001) 592–598.
- [52] Y. Sun, L. Song, Accurate determination of electrical potential on ion exchange membranes in reverse electrodialysis. Electrical potential on ion exchange membranes in reverse electrodialysis, Separations 8 (10) (2021) 170.
- [53] T.M. Sanders, M. Myers, M. Asadnia, G.A. Umana-Membreno, M. Baker, N. Fowkes, G. Parish, B. Nener, Description of ionophore-doped membranes with a blocked interface, Sens. Actuators B 250 (2017) 499–508.
- [54] B. Saliha, F. Patrick, S. Anthony, Investigating nanofiltration of multi-ionic solutions using the steric, electric and dielectric exclusion model, Chem. Eng. Sci. 64 (17) (2009) 3789–3798.
- [55] S. Abdu, M.-C. Martí-Calatayud, J.E. Wong, M. García-Gabaldón, M. Wessling, Layer-by-layer modification of cation exchange membranes controls ion selectivity and water splitting, ACS Appl. Mater. Interfaces 6 (3) (2014) 1843–1854.
- [56] O. Rybalkina, K. Tsygurina, K. Sabbatovskiy, E. Kirichenko, V. Sobolev, K. Kirichenko, Dependence of electrochemical properties of MK-40 heterogeneous membrane on number of adsorbed layers of polymers, Membranes 12 (2) (2022) 145.