



Selective recovery of silver from copper impurities by electro dialysis: Tailoring monovalent selective cation exchange membranes by monomolecular layer deposition

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ABSTRACT

Selective recovery of silver from secondary resources enriched with copper impurities is a well-known challenge but is urgently needed by the industry. This study addresses the challenge by developing a highly efficient monovalent selective cation exchange membrane (CEM) with a specifically tailored polyelectrolyte deposition, enabling efficient $\text{Ag}^+/\text{Cu}^{2+}$ separation in electro dialysis. Based on the $\text{Ag}^+/\text{Cu}^{2+}$ separation mechanism in electro dialysis, a selected polyelectrolyte, polyethyleneimine (PEI), was deposited on a standard CEM as a monomolecular layer with precisely controlled polymer chain stretch patterns and optimized morphologies. The effects of deposition conditions, such as solution pH and ionic strength, were studied to ensure the desired surface properties. The selectivity performance of the developed membranes was tested using an equimolar binary mixture; a high $\text{Ag}^+/\text{Cu}^{2+}$ selectivity of > 20 was documented, exhibiting superior selectivity performance compared to commercial monovalent selective CEMs.

1. Introduction

Precious and noble metals are naturally available rare elements, namely silver, gold, and the six platinum group metals, possessing high economic value due to their scarcity, wide use in different industrial-based applications, and superb chemical properties against oxidation and corrosion [1]. Among them, silver stands out as the most versatile precious metal due to its outstanding electrical and thermal conductivity and durability, and biocompatibility, contributing to various uses in diverse industries, such as catalysts, electronic devices, jewellery materials, and medical uses [2]. However, with the progress of worldwide industrialization, the high demand and rarity of silver have led to its rapid depletion, but the earth's crust contains silver only in finite amounts, making silver recycling from used sources urgent and imperative [3]. Therefore, the current focus of silver recovery has been directed to the electrorefining of the secondary sources of silver, including copper anode slime, scrapped electronic devices, and composite transistors [4]. However, these materials contain a large number of copper metals, causing continuous accumulation of copper ions

during the refining process, decreasing the purity of silver ions. Thus, a pre-treatment step is needed to ensure that silver streams for recycling are free from copper impurities.

Electrodialysis is a membrane technology, often used for the treatment of metal-contaminated solutions, relying on an electric field-driven migration of anions across an anion exchange membrane (AEM) and cations across a cation exchange membrane (CEM) [5]. Electro dialysis can achieve excellent selective recovery by functionalizing ion exchange membranes (IEMs), enhancing affinity with the target species, or optimizing the applied electric current and flow rate to facilitate the migration of target ions [6–9]. In addition, a huge volume of effluents with dilute concentrations of target ions can be treated in a short time [10]. Electro dialysis can also avoid additional chemicals and solid waste generation, emerging as an ecologically favorable option for selective recovery of silver, exhibiting reduced environmental impact [5,6,11].

Electrodialysis has been utilized to recycle and remove various metal ions [12–16]. However, the application of electro dialysis in the recovery of precious metals remains rare. There exists a significant need for endeavors in developing selective IEMs to achieve the desired recovery of

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precious metals, in particularly, silver. Güvenç et al. [17] reported the removal of silver ions both in a model solution and from electroplating rinse water using two different types of standard CEMs in a batch electro-dialysis. Full removal of silver ions was accomplished by applying the optimized voltage, demonstrating a proof-of-concept electro-dialysis process for silver recovery. However, the investigation into selective recovery of silver remains unexplored and is necessary for practical applications to meet industrial demands.

To the best of the authors' knowledge, only two electro-dialysis studies on selective separation of silver from divalent cations has been documented, and both involve the utilization of anionic chelating agents in the metallic feed solution to form complexes with the metallic species; thus, no monovalent selective membranes were applied. Cherif et al. [18] investigated the separation of silver from zinc and copper ions using ethylenediaminetetraacetic acid (EDTA). Due to the superior chelating affinity of EDTA for copper and zinc in comparison to silver, resulting in the formation of negatively charged complexes involving divalent cationic species, the migration of silver and chelated metals occurs in opposing directions, thereby accomplishing a notably selective separation. Similarly, Frioui et al. [19] examined the selective recovery of silver ions from zinc through the same hybrid electro-dialysis technique, employing various chelating agents. A highly selective recovery rate was achieved at optimal pH values, where the metal ion-ligand complex carried a negative charge. Although chelating agents selectively separate silver from various metal impurities, their low mobility, limited capacities, and pH-dependent chelation efficiency hinder current effectiveness, raising concerns for their viability in concentrated acidic effluents. Given the limitations of existing technologies for silver recovery, a promising strategy is required to meet stringent environmental demands while attaining high recovery rates.

Applying monovalent selective CEMs can provide a more effective approach [7,12,20]. Developing membrane with aligned characteristics specifically tailored for the targeted ions is crucial for achieving the desired selectivity. Forming an opposite charge and dense layer on the CEM surface through various active layers can offer outstanding selective separation properties, restricting the transfer of multivalent cations through the membrane due to a strong electrostatic repulsion and top-layer tightness [21–23]. Polyethyleneimine (PEI) is one of the most widely used polyelectrolytes for shaping the desired surface properties due to its ability to modify its degree of protonation and structure through deposition conditions (such as pH and ionic strength) [24,25]. Several techniques have been utilized for the modification of CEMs with PEI, including layer-by-layer deposition, chemical bonding, and electro-adsorption for metal separation, such as $\text{Li}^+/\text{Mg}^{2+}$ and $\text{Na}^+/\text{Mg}^{2+}-\text{Ca}^{2+}$ [26–30]. Additionally, PEI has also been used as a chelating agent in metal feed solutions for the separation of various transition elements from alkaline ions or acid [31–33].

Despite achieving the desired selectivities, the reported techniques have significant disadvantages. Layer-by-layer deposition is time and material-consuming and has layer detachment risks. Electrodeposition involves complex equipment and results in membrane surface entanglement, increasing ion permeation resistance [30,34,35]. Chemical bonding might require cross-linkers, applying harsh chemicals, and adding complexity and energy demands. On the other hand, single-layer deposition offers precise control over layer thickness and properties, which is advantageous when specific surface properties or functionalities are needed. Moreover, research addressing the relationship between structure and property, specifically concerning the influence of PEI on surface functionality with a strong preference for monovalent selectivity, is still in its early stages. The feasibility of utilizing PEI with precise surface tuning for the recovery of precious metals remains unexplored, which holds huge potential. The existing research gaps have inspired us to explore the influence of individually designed PEI layer on $\text{Ag}^+/\text{Cu}^{2+}$ separation in electro-dialysis, which, to the author's knowledge, has barely been reported through any PEI deposited membranes or monovalent selective CEMs.

Hence, this study aims at separating silver ions from effluents containing enriched copper ions impurities in electro-dialysis by specifically tailoring a monovalent selective CEM, enabling highly efficient $\text{Ag}^+/\text{Cu}^{2+}$ separation. A monomolecular layer of PEI under optimized deposition conditions was deposited on a commercial CEM for desired surface properties that can maximize the metal selectivity with low ion transport resistance. The patterns of the polymer chain stretch and charge groups of the deposited PEI were precisely controlled with optimized morphologies. Advanced surface analytical methods were used to characterize the modified membranes and establish correlations with their transport behaviour. To prevent potential metal precipitation resulting from the chelation ability of metal ions with PEI, the pH of the feed solution was adjusted to below 3. The monovalent selectivity performance of modified CEMs was tested with an equimolar mixture of silver and copper ions, exhibiting excellent selectivity and silver ion flux. Additionally, the monovalent selectivity of the CSE-WS CEM was investigated for comparison. The stability of the modified layer in an acidic environment was assessed to ensure the long-term viability of the membranes.

2. Materials and methods

2.1. Materials

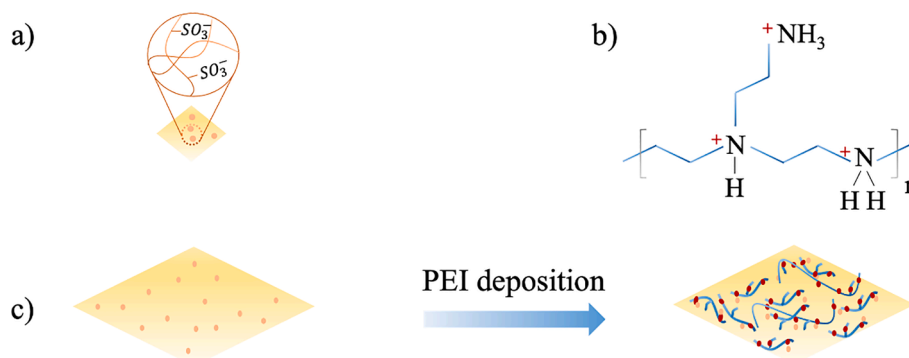
Ammonium nitrate (NH_4NO_3) was used to treat membranes for the electro-dialysis process. PEI ($M_w = 750,000$ Da) was used as a cationic polyelectrolyte coating material. The ionic strength and pH of the polyelectrolyte solutions were adjusted by sodium chloride (NaCl), sodium hydroxide (NaOH), and hydrochloric acid (HCl). Nitric acid (HNO_3) was used to fix the pH of the feed solution and test the chemical stability of the modified layers. Methylene blue (MB) was used for staining experiments. To test the selectivity performance, silver nitrate (AgNO_3) and copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) were used as the source of monovalent and divalent cations. Sodium sulfate (Na_2SO_4) was used as a rinse solution in the electro-dialysis stack. All the above chemicals were purchased from Aldrich, Germany. CMV (Selemion, Japan) and monovalent selective CSE-WS (Neosepta, Japan) were used as CEMs, while PC Acid 60 (PC Cell GmbH, Germany) was used as AEM in electro-dialysis tests.

2.2. Surface modification of the CEMs

PEI was used as a polycation to deposit the surface of the CMV CEM that includes fixed sulfonic groups in its structure (Scheme 1a,b). The unmodified CMV membrane was kept in a holder to limit the film forming on only one side of the membrane. The deposition of the PEI layer was performed at a pH of 3, 5, or 7. The concentration of PEI was fixed at $1.0 \text{ g}\cdot\text{L}^{-1}$. Each PEI solution was prepared for ionic strengths of 0 M and 0.5 M NaCl. The feed of the different membranes coated by PEI at various deposition conditions is given in Table 1. PEI deposition was performed statically for 60 min (Scheme 1c). After the deposition, the membrane surface was rinsed with deionized water for ~ 60 s to remove excess and weakly adsorbed polyelectrolytes. Modified CEMs are named CMV_PEI_x_y , where x represents the deposition pH, and y is the ionic strength.

2.3. Membrane characterization methods

X-ray photoelectron spectroscopy (XPS) (Axis Ultra DLD, Kratos Analytical) was used to characterize the chemical composition and atomic concentration of both the commercial and all PEI-modified membrane sets by analyzing the intensity of XPS peaks emitted from the samples. The membrane surface composition was examined to quantitatively determine the deposited layers. The nitrogen-to-sulfur ratio in the analyzed membranes, corresponding to the elements in the PEI layer and support, respectively, was employed to compare layer



Scheme 1. a) The CMV membrane with pendant sulfonic groups; b) the repeating unit of branched-pei; c) the deposition of PEI on the CMV membrane.

Table 1
The modified membranes at different PEI deposition conditions.

Unmodified membrane	pH	Ionic strength	Modified membrane
CMV	3	0 M NaCl	CMV_PEI_3_0
		0.5 M NaCl	CMV_PEI_3_0.5
CMV	5	0 M NaCl	CMV_PEI_5_0
		0.5 M NaCl	CMV_PEI_5_0.5
CMV	7	0 M NaCl	CMV_PEI_7_0
		0.5 M NaCl	CMV_PEI_7_0.5

growth among all modified membranes. Additionally, the chemical state of the nitrogen was also determined to distinguish between neutral and positively charged nitrogen in the modified membranes. The ratio of protonated nitrogen to sulfur was used to evaluate the quantitative surface charge of the membranes.

Color intensity measurements were performed with MB dye to give complementary information regarding the qualitative surface charge of the unmodified and modified membranes [36]. The CEMs were kept in 10⁻³ M of MB solution. The solution pH of MB was adjusted by the addition of HCl or NaOH to 7 or 2.3, which was positively charged under its isoelectronic point (\approx pH 8) [37]. Then, the stained membranes were rinsed with deionized water until the water became colorless to ensure weakly attached dye molecules were removed from the membrane surface. The color intensity of the membranes was measured with a Spectrometer using AvaSoft software.

Field emission scanning electron microscopy (FESEM) (Apreo, FEI) was used to characterize the surface topography of unmodified and modified CEMs. Before the analysis, membrane samples were cut into small pieces and dried at 25 °C under a vacuum. Then, the SEM samples were fixed on a sample holder with single-sided copper tape. Atomic force microscopy (AFM) (Dimension Icon, Bruker Dimension) was used to indicate the surface roughness of the dried membranes. PeakForce tapping mode was used to scan a 5 × 5 μm surface using a ScanAsyst Air probe. All images were corrected by a fitting procedure to apply the same procedure to the compared samples.

2.4. Water uptake and water contact angle

The difference in weight of dry and wet membrane samples was determined by water uptake measurements. First, membrane samples were cut into smaller pieces and dried in an oven under a vacuum at 60 °C for 24 h. Then, the weight of the dried samples was measured. Subsequently, the samples were immersed in deionized water for another 24 h at room temperature. The weight of the wet membrane samples was measured right after removing the residual water. Water uptake values were determined by the following equation (1):

$$\text{Water uptake (\%)} = \frac{(W_{\text{wet}} - W_{\text{dry}})}{W_{\text{dry}}} \cdot 100 \quad (1)$$

where W_{wet} and W_{dry} are the weights of the wet and dry CEM samples, respectively.

The surface hydrophobicity of unmodified and modified membranes was determined by water contact angle measurements using an optical tensiometer (T330, Biolin Scientific). The dried membranes were fixed on a glass slide before the measurement. Measurements were performed four times with 4 μL deionized water droplets for each membrane.

2.5. Electrochemical characterization of the membranes

The current–voltage curves of the CMV, CSE-WS, and the selected PEI-modified membrane were determined in a four-electrode configuration. The setup for recording current–voltage curves was illustrated in our previous paper [9]. The working sense and counter sense were connected to the stack electrodes while mercury-sulfate reference electrodes (Gamry) were in the rinse solutions. The respective CEM was sandwiched between two AEMs in a crossflow electro dialysis stack. A 10 mM AgNO₃/Cu(NO₃)₂ · 3H₂O mixture was used as a feed stream for the diluate and concentrate compartments, while 0.25 M sodium sulfate solution was used in the rinse compartments at the electrodes. The pH of the feed solution was adjusted to 2.3 by the HNO₃ solution, which was the feed pH for the selectivity measurements. The solutions were circulated at a flow rate of 120 mL·min⁻¹ in all the compartments. During the test, the current was increased stepwise while each step was held for 30 s, and data were recorded every 0.25 s. The current–voltage curves measurement of the membranes was also carried out without the pH adjustment of the feed solution (generating a pH value of around 5 for a 10 mM binary mixture) to demonstrate the effect of the solution pH on the current–voltage characteristics. The raw data for current–voltage characteristics of all used membranes measured at two different feed pH values with respect to time is given as [supplementary information \(SI\) \(Figure S1\)](#).

The conductivity of CEMs was measured using electrochemical impedance spectroscopy. All membranes were equilibrated for 24 h in a 10 mM AgNO₃/Cu(NO₃)₂ · 3H₂O solution adjusted to pH 2.3 using HNO₃. A detailed explanation of the method and the measurement are given and illustrated in the [supplementary information \(Figure S2 and Figure S3\)](#). The resistance per length of thickness of the membrane obtained from the impedance measurements was used to calculate the membrane conductivity by the following equation (2):

$$\frac{R}{l} = \frac{1}{\kappa A} \quad (2)$$

where R (Ω) is the resistance, l (cm) is the membrane thickness, A is the membrane area (cm²), and κ is the membrane conductivity (mS · cm⁻¹).

2.6. Monovalent cation selectivity measurements

Prior to the electro dialysis tests, the commercial AEMs and CEMs stored in 0.5 M NaCl solution were immersed in 1 M ammonium nitrate solution for 60 min to replace excess chloride in the membranes with nitrate ions to eliminate the possible silver chloride precipitation during the electro dialysis process. Then, the membranes were rinsed with deionized water, followed by immersion in a fresh concentrate ammonium nitrate solution for another 60 min. After rinsing the membranes with deionized water, the rinse solution was titrated with 0.1 M of AgNO_3 solution to ensure no AgCl precipitate was observed.

The monovalent selectivity tests of the CEMs were conducted by a Micro BED electro dialysis device (PCCell GmbH, Germany). Four chambers are present in the membrane stack: one concentrate, one diluate, and two electrode chambers (Fig. 1). CEMs were placed in the middle of the cell to investigate the transfer of cations from diluate to concentrate chambers. Commercial end-AEMs were used at both ends of the stack to limit the interference of the rinse solution with the feed solution. $3.5 \text{ mA}\cdot\text{cm}^{-2}$ current density was generated through the membranes having an effective area of 6 cm^2 . The applied current density was determined based on the current–voltage characteristics of the membranes. The diluate and concentrate chambers were fed with a 120 mL 10 mM mixture of AgNO_3 and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ applying the circular flow rate of $120 \text{ mL}\cdot\text{min}^{-1}$. 100 mL 0.25 M Na_2SO_4 electrolyte solution was circulated through electrode chambers, and the measurement lasted for 120 min. The pH of the feed solution was adjusted to 2.3 by the HNO_3 solution to prevent metal precipitation on the PEI-modified membrane surface. During the electro dialysis process, 3 mL samples were taken from both chambers every 30 min, leading to a total volume decrease of less than 8 % in each batch. The content of the silver and copper ions in the samples was determined by a microwave plasma-atomic emission spectrometer (Agilent 4210). The selectivity $[P_B^A]$ between silver and copper ions was obtained from equation (3):

$$P_B^A = \frac{J_A C_B}{J_B C_A} \quad (3)$$

where J_A and J_B ($\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$) are the fluxes of the components A (silver) and B (copper), while C_A and C_B ($\text{mol}\cdot\text{L}^{-1}$) are the average concentrations on the diluate side of the membranes. The ionic flux through the membranes was determined using equation (4):

$$J_A = \frac{V \frac{dC_A}{dt}}{A} \quad (4)$$

where V (L) is the feed solution volume, dC_A ($\text{mol}\cdot\text{L}^{-1}$) is the concentration change of component A, and A (m^2) is the active area of the membrane. The specific energy consumption (E_m) in the membrane per mole of the transported cations and current efficiency (η) were

calculated according to the relations (5) and (6):

$$E_m = \frac{\int U_m \cdot I \cdot dt}{(C_0 - C_t) \cdot V} \quad (5)$$

$$\eta (\%) = \frac{z \cdot F \cdot (C_0 - C_t) \cdot V}{N \cdot I \cdot \Delta t} \cdot 100 \quad (6)$$

where I (A) is the applied current, U_m (V) is the voltage drop across the cell, and C_0 and C_t are the concentrations of the cations initially and at a specific time t , z is the absolute valence of silver ions, F is the Faraday constant ($96,485 \text{ C}\cdot\text{mol}^{-1}$), and N is the number of repeating units in the electro dialysis stack ($N = 1$).

3. Results and discussion

3.1. Membrane surface characteristics

3.1.1. PEI adsorbed amount

PEI is a weak polyelectrolyte, which enables control over its protonation degree and the final structure by solution pH and salt. The salt and pH determine the extent of polyelectrolyte adsorption, its charge density on the membrane surface, and the conformation of the polyelectrolyte, affecting the permeability of the metal ions through the PEI-modified membrane. The surface characteristics of commercial CEMs and membranes modified by PEI at various deposition conditions were investigated by XPS measurements.

The atomic concentration ratio between nitrogen and sulfur (N/S) in the membranes is used to demonstrate the layer growth [26,38] (Fig. 2). The CMV membrane carrying the fixed sulfonic groups in its structure yielded the lowest N/S ratio. It is noteworthy that the nitrogen content in the membrane is related to the remaining nitrogen-based additive during the fabrication process [39]. PEI modification increased the N/S ratio, revealing the successful deposition on the CMV membrane. The membrane modified by PEI at pH 7 demonstrated a higher N/S ratio compared to those modified at lower pH values when the ionic strength was kept constant. The higher N/S value confirms more attached amine groups on the membrane surface. The reason is that when the PEI is in a neutral pH region ($\text{pH} = 7$), the electrostatic barrier throughout the PEI segment is relatively low due to the low protonation degree. This, in turn, causes the PEI segments to fold, which results in a coiled structure possessing a lower area and more prone to attach to the membrane surface, yielding higher adsorption [40–42]. Decreasing the deposition pH to 5 slightly reduced the N/S ratio, suggesting less PEI adsorption, which is attributed to the increasing dominance of segment-segment repulsion among PEI monomers when its protonation degree is increased [40,41,43]. The repulsion becomes stronger at pH 3, at which PEI occurs in its most extended structure due to the developed

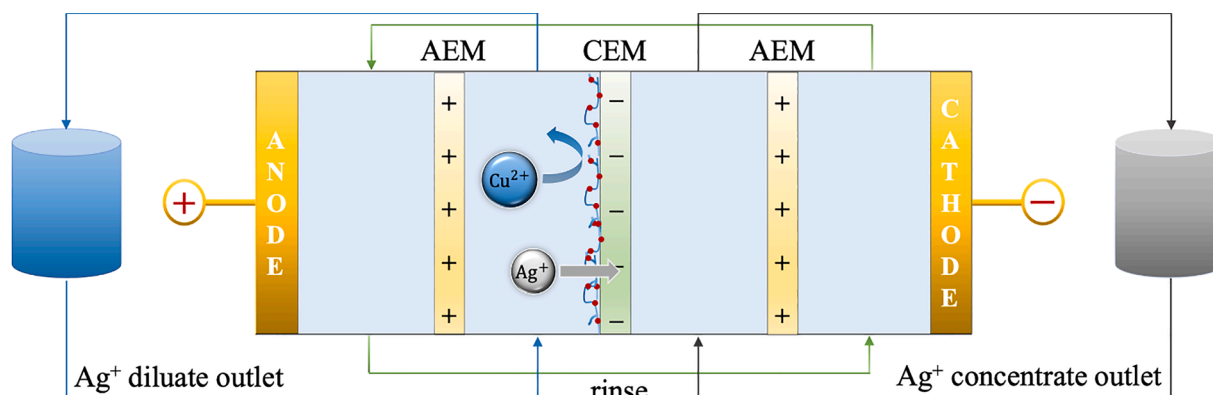


Fig. 1. Membrane stack assembly in an electro dialysis cell. The difference in the size of the cations is based on their hydrated sizes. CEM represents the PEI-modified membrane.

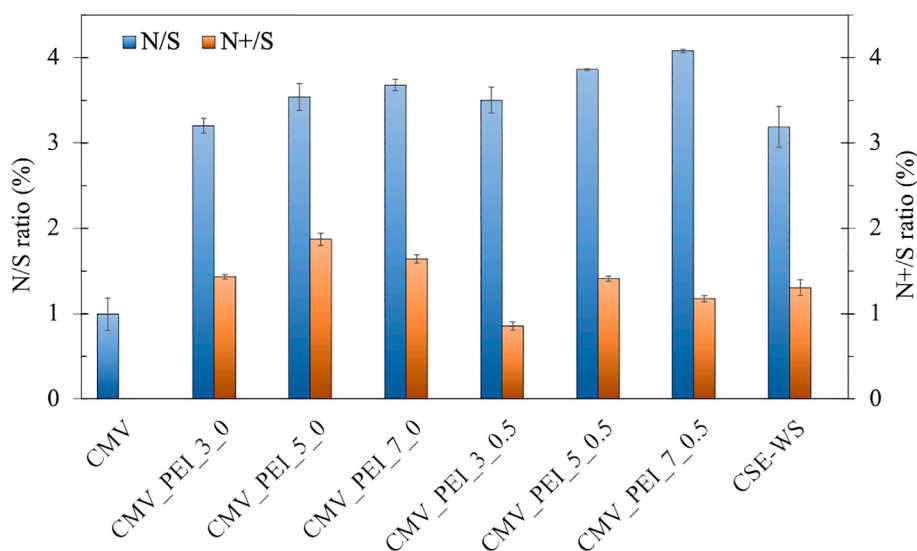


Fig. 2. N/S and N⁺/S ratios of the commercial and PEI-modified CEMs.

electrostatic barrier along the segment. This led to a strong repulsion among the individual PEI segments, causing a drastic decrease in the adsorbed amount [40,41,44].

The effect of ionic strength on the adsorbed amount of PEI is also represented in Fig. 2. Increasing the ionic strength from 0 M to 0.5 M at fixed pH values increases the N/S ratio, implying higher adsorption. Simply, a high salt concentration screens the charges on PEI segments and results in a smaller radius of gyration, facilitating more PEI monomers to attach to the same membrane surface area [40,45]. The radius of the gyration value of the PEI chain in 0.5 M NaCl was reported to be consistently lower than that in salt-free solutions at any pH value [46]. Moreover, high ionic strength can eliminate the segment-segment repulsion effect by balancing the protonated amines on PEI with the counter-ions of salts but induces surface-segment attractions, triggering greater adsorption [24,40,47]. XPS measurements show that PEI adsorption increases with decreased protonation degree of the PEI layer after increasing either pH or ionic strength.

3.1.2. Membrane charge densities

Fig. 2 also reveals charge densities for each membrane by the ratio of the protonated nitrogen to the sulfur content (N⁺/S) of the membranes. The deconvolution of N 1s XPS spectra of the membranes is given in Figure S4. The deposition pH influenced the extent of charge density of the membranes differently. The N⁺/S ratio of the CMV_PEI_3_0 membrane was found to be lower than the membranes modified at higher pH values in the absence of salt, suggesting less surface charge density. Increasing the deposition pH to 5 displayed the highest N⁺/S ratio, indicating more available positive charges on the surface that can be ascribed to the excess adsorbed amount of PEI compared to the deposition at pH 3. However, a further increase in deposition pH to 7 presented a lower N⁺/S ratio compared to the PEI deposition at pH 5, which stems from the fact that the adsorbed amount slightly increases after increasing deposition pH to 7 but the protonation degree of branched-PEI at pH 7 (~20 %) is much lower than at pH 5 (~45 %), leading to a lower surface charge density [48]. Nevertheless, the modified membrane by PEI at pH 7 displayed a higher N⁺/S ratio compared to that at pH 3, due to the much higher adsorption, giving rise to providing more free charge on the membrane surface. On the other hand, the addition of salt to the PEI solution lowered the charge densities despite much higher adsorption, while the trend of the N⁺/S ratio for the membranes with deposition pH remained the same. It is attributed to the decrease in ionization degrees of the polyelectrolyte units by the adsorption of large amounts of counter-ions on free ionic groups on the PEI backbone

[49,50]. Meanwhile, the monovalent CSE-WS membrane exhibited a similar N⁺/S ratio compared to the membranes modified in the presence of salt, suggesting a positive surface charge.

The qualitative surface charge of the unmodified and modified membranes was also determined by the color intensity measurements (dye staining method) after the membranes were exposed to the MB solution (Fig. 3). When the CMV membrane surface was unstained, the color intensity value was the minimum (12.7 ± 0.3). However, after MB staining, it yielded the maximum color intensity value (-21.9 ± 0.3) due to high electrostatic attraction between the positively charged dye molecules and the negative membrane surface. Notably, more dye adsorption brings about a higher negative color intensity value. It is essential to note that similar color intensity values were obtained for the stained CMV membrane regardless of the MB solution pH, demonstrating that the membrane net surface charge was not affected by the pH of the environment.

The color intensity values for all PEI-modified membranes were found to be lower than the stained CMV membrane due to the presence of protonated amine groups, allowing less attachment of MB. The difference in the magnitude of color intensity for PEI-modified membranes is decided by polyelectrolyte deposition conditions. The membranes prepared from PEI solutions at higher ionic strength demonstrated higher color intensities than those deposited in the absence of salt ions, indicating fewer available positive charges on the surface of the modified membranes containing salt; hence, more binding of MB is observed. The more MB attachment can be attributed to the charge screening on PEI, leading to a lower positive surface charge as presented by the XPS measurements [50–52]. It should be noted that the salt-added solutions of PEI resulted in greater adsorption despite having fewer available positive sites. It is because a minimum charge density is enough for polyelectrolyte deposition to occur, which is driven by entropy gain accompanied by a partial release of counter-ions, lowering the counter-ion concentrations within the deposited film [52,53].

The deposition pH also affected the adsorbed amount of MB on the surface. The color intensity was the lowest for the membrane deposited at pH 5 at the zero-salt limit, proving the most available free positive charges on the membrane surface. These findings agree well with the results obtained by XPS measurements. Another important note was that when MB pH was reduced to 2.3, color intensity values of the modified membranes approached the value obtained for unstained CMV, expressing less MB adsorption. The explanation can be the further protonation of the attached PEI in the acidic solution, preventing more MB molecules from adsorbing to the surface [25,41,42]. It is interesting that

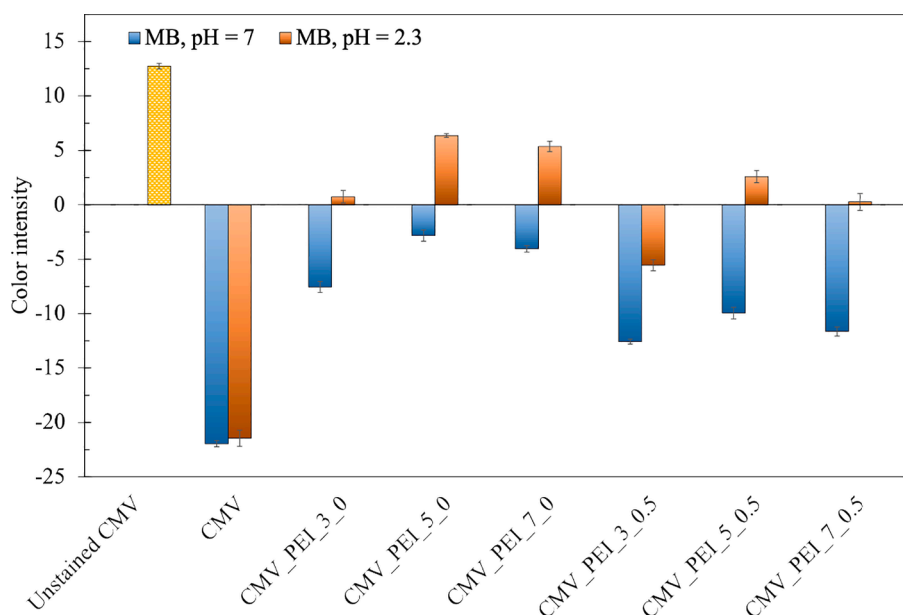


Fig. 3. Color intensity values of the commercial and PEI-modified CEMs. The higher the negative value, the greater the color intensity value is.

CMV_PEI_7_0 displayed less surface charge than CMV_PEI_5_0 in the acidic MB solution despite having more protonation possibility due to having more adsorbed PEI. This might be explained by the incomplete ionization of the amine groups as a result of a coiled and thicker structure of the layer at pH 7, reducing the contact area and causing less positive charge [54]. It can be deduced from the results of XPS and staining measurements that PEI deposition at pH 3 is limited by adsorption due to segment-segment repulsion, while the deposition at pH 7 is restricted by the charge density despite higher adsorption, suggesting that deposition at pH 5 facilitates high enough adsorption and free positive charges on the membrane surface.

3.2. Morphological characteristics

The changes in topographic morphology of the membranes depending on the polyelectrolyte deposition conditions were evaluated as the root-mean-square (R_q) roughness value by AFM measurements (Fig. 4). The PEI layer formation based on the results of the surface characterizations is illustrated in Scheme 2. The unmodified CMV membrane displayed the lowest roughness value, confirming its smooth and flat surface. The surface roughness of the modified membranes (between 3.6 and 6.3 nm) was higher compared to the unmodified membrane (3.23 nm), which is in the range of the hydrodynamic radius of a monomolecular layer of branched-PEI [55]. Similar findings were reported by McAloney et al. for polydiallyldimethylammonium chloride polycation with a molecular weight similar to PEI [56]. The roughness differs depending on the polyelectrolyte deposition conditions and the consequently different single molecular chain settlement patterns (Scheme 2). The membrane modified by PEI at pH 3 and the zero-salt limit displayed only a slight increase in roughness compared to the unmodified membrane, which can be explained by the flat configuration of the PEI monomers at a low pH [57]. The membranes modified at higher pH values displayed higher surface roughness due to the chain transition from a flat to a coiled conformation, increasing film thickness and roughness (Scheme 2a) [40,57]. When salt ions were included in the PEI solution, even higher roughness values were obtained as a result of the formation of a looper, thicker, and more rough structure due to the charge screening (Scheme 2b) [47,56]. Results indicate that the roughness increases as the deposition pH and ionic strength increase.

The deposition of the PEI layer was visually verified through the analysis of the surface morphology images of unmodified and modified

CEMs by FESEM. Fig. 5 shows the surface topography images of the CMV as well as the selected CMV_PEI_5_0 and CMV_PEI_5_0.5 membranes with magnified versions at the top. From the images, the commercial CMV membrane demonstrated a smooth and defect-free surface, whereas the PEI-modified membranes displayed polyelectrolyte segments, revealing the successful coating on the unmodified membrane. The modified membrane at the zero-salt limit (CMV_PEI_5_0) displayed a smoother surface (small nodules forming throughout the membrane) than those modified at high ionic strength, the surface of which presented a rougher structure. The different surface morphology can be attributed to the more coiled structure of PEI in the presence of salt, causing a thicker and more rough structure [47,56].

3.3. Water uptake and hydrophilicity

Management of water uptake in polymeric membranes is critical for controlling the dimensional stability and selectivity performances of the membranes. The water uptake mainly depends on the nature of the polymeric material as well as the charge density of the membrane [58]. The water uptake values of the commercial and modified membranes are represented in Fig. 6. The CSE-WS membrane presented the highest water uptake among all tested CEMs, being the most hydrophilic membrane, while the CMV membrane displayed a lower value. The water uptake values underwent a significant decrease after the modification of the PEI layer having a hydrophobic backbone [24]. Each modified membrane varied in water uptake values due to the differences in polyelectrolyte deposition conditions, providing distinct surface properties. The CMV_PEI_3_0 membrane had the highest water uptake value among all modified membranes. This was attributed to the elongated structure of PEI, accommodating more water molecules [59]. Oppositely, the membranes modified by PEI at higher pH values presented lower water uptake values. This was ascribed to the increased density of the ethylene backbone and unprotonated parts of PEI on the membrane surface due to higher adsorption, sharing solvation shells from its neighbours [59]. Interestingly, the water uptake value of CMV_PEI_7_0 was higher than CMV_PEI_5_0 despite its lower surface charge with more adsorbed PEI. The reason is explained by the more coiled-structured PEI on the surface resulting in a wider gap between the attached segments that allowed more water molecules to penetrate the inner part of the layer and interact with more functional units [25]. Adding salt to the PEI solution decreased the water uptake values of the

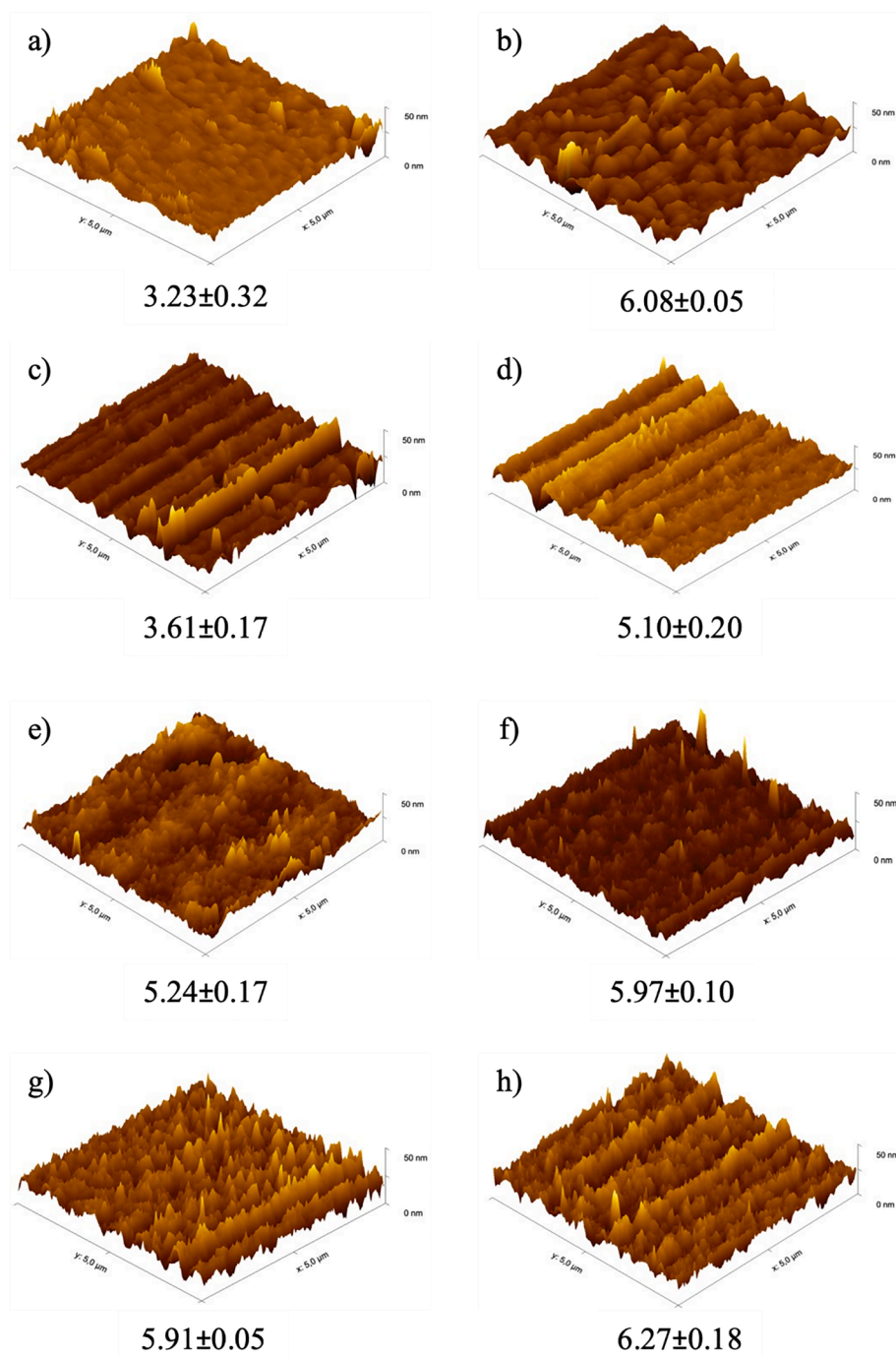
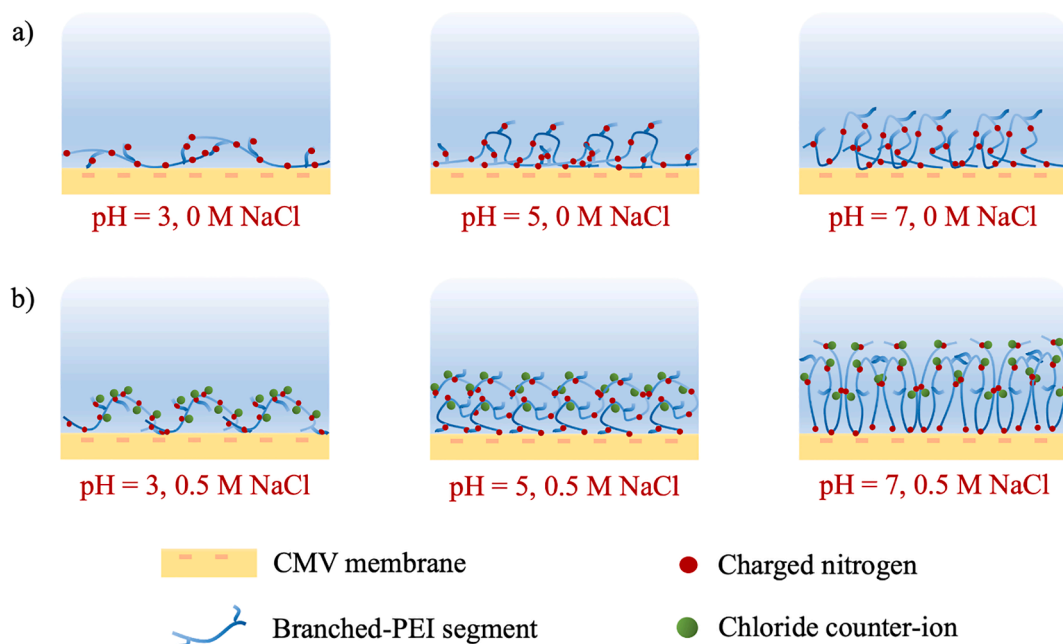


Fig. 4. AFM images of CEMs; (a) CMV; (b) CSE-WS; (c) CMV_PEI_3_0; (d) CMV_PEI_3_0.5; (e) CMV_PEI_5_0; (f) CMV_PEI_5_0.5; (g) CMV_PEI_7_0; (h) CMV_PEI_7_0.5. The images are 5 × 5 μm. The vertical scale bar for all the images is 50 nm. The values represent the roughness in nm.

membranes due to the reduced charge density holding fewer water molecules [50]. Furthermore, less surface charge allows stronger hydrophobic interactions along the PEI segment to hold the chain in compact conformations, covering the membrane surface better and preventing the water molecules from penetrating through the layers [59].

The surface hydrophobicity of the membranes was investigated by water contact angle measurements. As it is expected, the CMV and CSE-WS CEMs represented much lower contact angle values due to their ability to hold more water molecules, as suggested by the water uptake measurements. Incorporating a PEI layer to the surface increased the water contact angles and differed depending on the deposition

conditions. For instance, the membrane modified by PEI solution at pH 3 without salt resulted in the lowest water contact angle value among all modified membranes. Given that PEI carries the amines in their most protonated form at the lowest pH, it provides a more hydrophilic surface due to its hydrophilic nature [55]. When the deposition pH was increased from 3 to 5, the water contact angle also increased. Greater adsorption at pH 5 provided a more hydrophobic ethylene-rich backbone and the unprotonated portion of the segments, increasing the hydrophobicity of the membrane. Expectedly, when the PEI deposition pH was 7 at the zero-salt limit, the contact angle kept increasing due to more adsorbed PEI and fewer free-charged units. The surface hydrophobicity of the membranes increased even more after adding salt to the PEI



Scheme 2. Schematic representation of the PEI layer formation on the membrane surface at various deposition conditions; (a) PEI at pH 3 in the absence of salt is at its most protonated structure, leading to a rod-like shape and the least adsorbed amount due to the intra-chain repulsion of the segments. Increasing deposition pH to 5 and 7 lessens the electrostatic barrier and causes the PEI to fold, which results in a coiled structure possessing a lower area and higher adsorption; (b) the ionic strength screens the charge repulsion between PEI monomers, causing a smaller radius of gyration that facilitates more PEI monomer adsorption with a loopy structure and reduced charge density. The increase in deposition pH in the presence of salt results in more rough, thicker, and loopier structures.

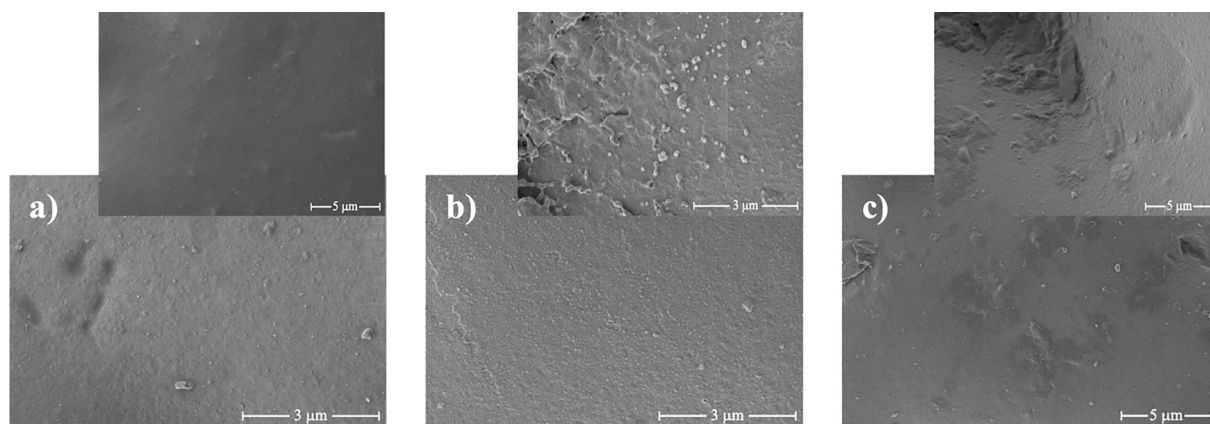


Fig. 5. FESEM images of CEMs; (a) unmodified CMV; (b) CMV_{PEI_5_0}; (c) CMV_{PEI_5_0.5}.

solution as a result of greater adsorption and a reduced charged density of the PEI monomers.

3.4. Electrochemical properties of the membranes

The current–voltage characteristics of electrodialysis stacks show a transition from pure ohmic (i.e., linear) behaviour to a current regime where the curve flattens with increasing voltage due to concentration polarization effects. To avoid energy inefficiencies, electrodialysis was performed at currents within the ohmic regime. However, the desalination rate is proportional to the applied current, which should therefore be high enough to enable desalination within a reasonable time frame. For this purpose, current–voltage curves of the CMV, CSE-WS, and CMV_{PEI_5_0.5} membranes were obtained and analyzed. The voltage value was plotted against the respective current density (Fig. 7).

The curve follows a linear trend in the ohmic region. The conductivities of the investigated membranes in 10 mM AgNO₃/Cu(NO₃)₂ · 3H₂O solution, adjusted to pH 2.3 using HNO₃, are shown in the

supplementary information (Figure S5). The membrane surface modifications do not significantly alter the membrane conductivity compared to the unmodified membrane, which was found to be around 1 mS·cm⁻¹. However, the CSE-WS membrane exhibited a conductivity of around 0.75 mS·cm⁻¹. The current–voltage characteristics also reveal a steeper slope for the unmodified CMV and CMV_{PEI_5_0.5} compared to CSE-WS, indicating higher resistance for CSE-WS. The difference in the slopes of CMV and CMV_{PEI_5_0.5} toward higher voltages is due to the increased resistance to copper ions for CMV_{PEI_5_0.5} as silver becomes depleted. The membrane selectivity ensures rapid silver removal, leaving copper behind, which can affect membrane conductivity. Furthermore, the results suggest that the proposed surface modification can be a viable method for producing silver-selective membranes without substantially increasing membrane resistance.

At increasing current densities, the curve flattens, indicating that the ion transport is limited by diffusion through the boundary layer due to insufficient diffusion rates of the ions compared to the availability of electrons, leading to increasing concentration polarization effects. This

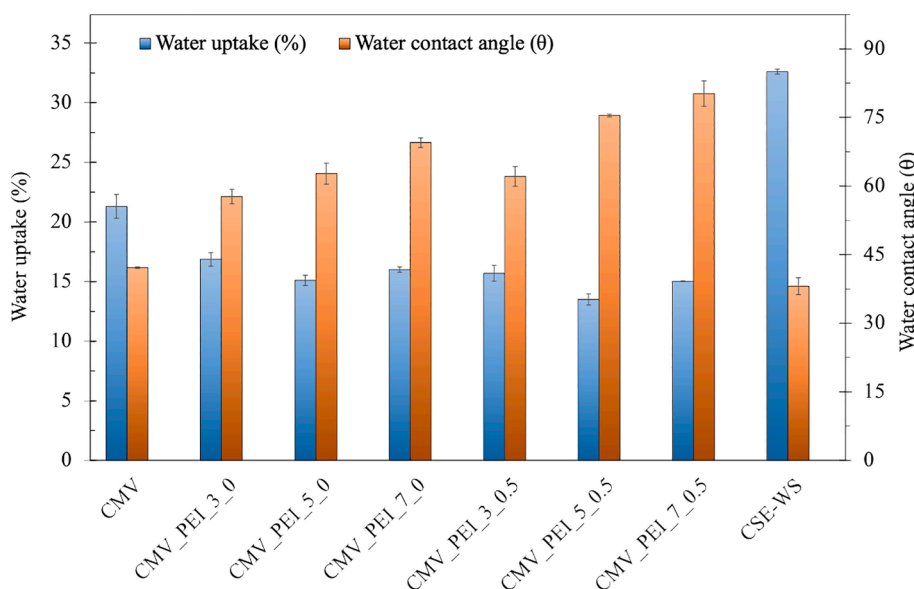


Fig. 6. Water uptake values of the commercial and PEI-modified CEMs.

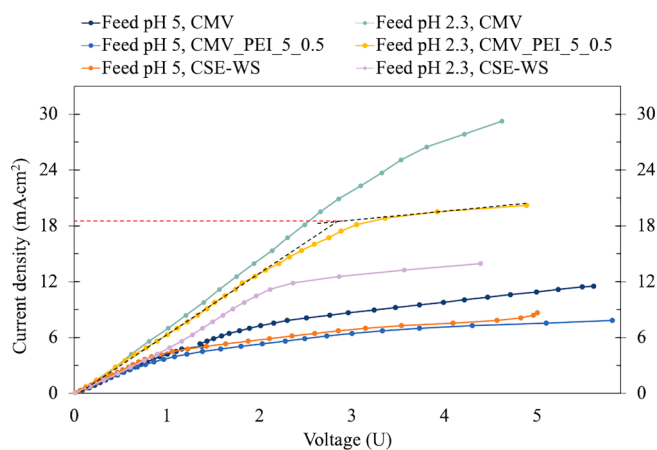


Fig. 7. The current–voltage characteristics of the commercial and PEI-modified CEMs.

results in increased resistance of the membrane system and undesirable side reactions (i.e., water splitting), causing energy efficiency and selectivity performance losses [9]. Hence, we took a measure of the maximum practical current as the limiting current before diffusion limitations get impractically high to avoid a drop in current efficiency and water dissociation and to operate electro dialysis economically, identified by the intersection of the tangents between the ohmic region and plateau region, as listed in Table 2. In literature, this value is also referred to as limiting current density [60].

The limiting current regions for CMV_PEI_5_0.5 and CSE-WS were reached earlier relative to CMV, which is attributable to the fact that applying monovalent selective membranes increases the concentration polarization effect by diminishing the migration rate of the ions.

Table 2
Current densities of the CEMs at the intersection points.

CEM	(mA·cm ⁻²) feed pH 5	feed pH 2.3
CMV	7.9	25.7
CMV_PEI_5_0.5	6.7	18.8
CSE-WS	5.9	13.3

Specifically, most of the copper ions are not allowed to pass through the PEI-modified and CSE-WS membranes as a result of electrostatic repulsion and dense structure, increasing the resistance of the membrane system. Among the modified membranes, the current–voltage characteristic was only determined for CMV_PEI_5_0.5, which exhibited the lowest copper ion flux, indicating high resistance to copper transport and necessitating the highest energy input. Consequently, the other PEI-modified membranes tend to reach the limiting current region later compared to CMV_PEI_5_0.5 because membranes with lower resistance have higher limiting currents. This relation is in agreement with the findings reported in the literature [61,62]. When the feed pH was 2.3, the current densities at the intersection points increased drastically, with a factor of 3.3 for CMV, 2.8 for CMV_PEI_5_0.5, and 2.3 for CSE-WS, respectively. The higher value at low pH is ascribed to the abundance of protons, which also carry charge down the electric potential gradient and help maintain ohmic behavior at the cost of current efficiency. The current density in the desalination experiments was chosen to be 3.5 mA·cm⁻², which was well below the limiting value for all membranes. However, the current density was further restricted by scaling occurring on the membranes at higher current densities due to the accumulation and precipitation of metals on the membrane surface facing the concentrate compartment.

3.5. Monovalent cation selectivity performances

The selectivity between monovalent and multivalent cations is mainly decided by the properties of the membranes applied. The developed PEI-modified membranes and a commercial CMV membrane were tested with the binary mixture of AgNO₃/Cu(NO₃)₂ · 3H₂O in electro dialysis for selectivity performance evaluation. The monovalent selectivity performance of the CSE-WS CEM was also investigated for comparison. Based on the current – voltage curves measurements, the electro dialysis experiments were performed at a constant current density of 3.5 mA·cm⁻². The pH of the feed solution was adjusted to 2.3 to prevent metal ions from scaling on the PEI-modified membranes. The flux and selectivity performances of all used CEMs are depicted in Fig. 8 and Fig. 9. The concentration changes used to calculate flux and monovalent selectivity are given as the SI (Figure S6-S13).

Fig. 8 reveals that the flux of copper ions (5.9 ± 0.6 nmol·cm⁻²·s⁻¹) was much higher than that of silver ions (3.4 ± 0.4 nmol·cm⁻²·s⁻¹) for the CMV membrane. The reason is that divalent copper ions can establish higher affinity with the fixed negatively charged sulfonic groups in

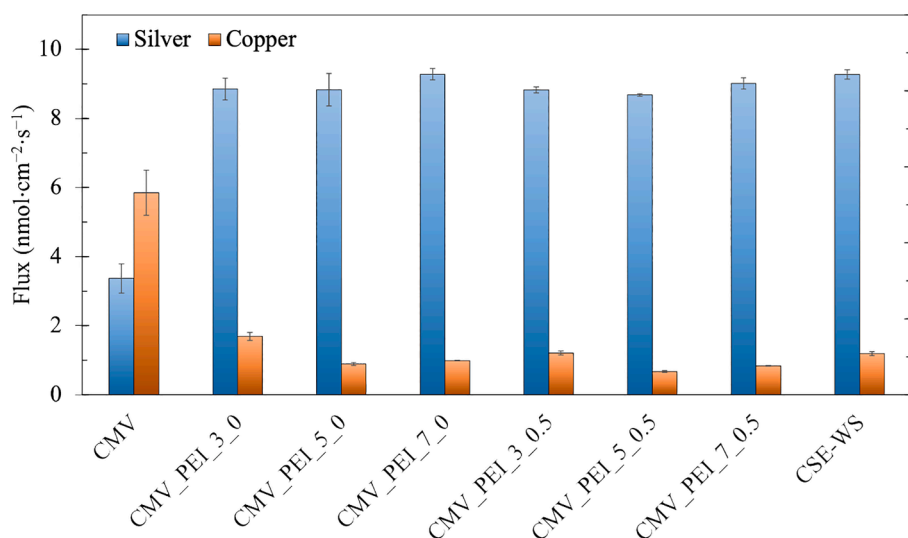


Fig. 8. The flux of the commercial and PEI-modified CEMs.

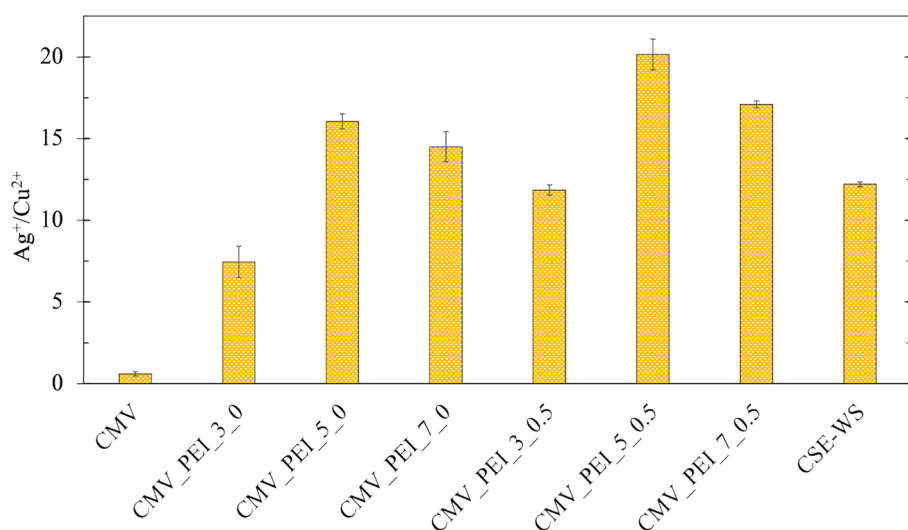


Fig. 9. Ag⁺/Cu²⁺ selectivity of the commercial and PEI-modified CEMs.

the CMV membrane due to a stronger Coulombic attraction force [19]. Moreover, the hydrophilic character of the CMV membrane provides wide enough hydrophilic entrances, allowing the passage of copper ions despite its big hydrated size. Therefore, ion permeation through the CMV membrane was in the order of Cu²⁺ > Ag⁺, hampering monovalent selectivity (Ag⁺/Cu²⁺ = 0.6 ± 0.1).

The ionic characteristics of silver and copper ions are given in Table 3, which seem to have played a key role in their permeation ability through the membranes. The findings indicated that the migration of cations through the modified membranes is substantially affected by the PEI deposition conditions that influence the final surface properties.

3.5.1. Effect of PEI solution pH

The surface of the CMV membrane was modified by PEI at various deposition conditions to achieve the selective separation of silver from

copper ions. A single-layer formation of PEI improved the monovalent ion selectivity drastically, as seen in Fig. 9. Notwithstanding, the selectivity performance of the membranes modified by the single PEI layer shows different behavior depending on the deposition conditions. The deposition pH was one of the primary effects, influencing the selectivity between cations. The membrane modified at pH 3 in the absence of salt reduced the flux of copper ions to 1.7 ± 0.1 nmol·cm⁻²·s⁻¹, while silver ion flux increased to 8.9 ± 0.3 nmol·cm⁻²·s⁻¹, enhancing the selectivity of Ag⁺/Cu²⁺ from 0.6 ± 0.1 to 7.5 ± 0.9 compared with the unmodified membrane. The improved selectivity proves the successful coating of PEI, altering the migration ability of cations through the membrane. Upon modification of the membrane with PEI, introducing a positively charged and compact surface layer engenders more potent repulsive forces and sieving effects against copper ions. Consequently, these effects lead to the preferential

Table 3

Ion characteristics of cations.

Cation	Ionic radius (Å) [63]	Hydrated radius (Å) [63]	Charge density (C·mm ⁻³) [64]	Hydration free energy (kJ·mol ⁻¹) [65]
Ag ⁺	1.26	3.41	15	-430
Cu ²⁺	0.72	4.19	116	-2010

displacement of copper ions from the membrane surface, resulting in a swap with silver ions. Hence, the modified membranes led to an increase in the current carried by silver ions, implying an impediment to the transport of copper ions, as described in [Figure S14](#). Nevertheless, the membrane modified by PEI at pH 3 yielded the lowest monovalent selectivity among all modified membranes, which can be attributed to the lower adsorption of PEI and surface charge ([Scheme 2a](#)), as shown by XPS measurements.

In contrast, membranes coated with PEI at higher pH values exhibited enhanced selectivity performance. For instance, increasing the deposition pH from 3 to 5 at the zero-salt limit led to a substantial increase in monovalent selectivity ($Ag^+/Cu^{2+}=16.1 \pm 0.5$), where the fluxes of silver and copper ions were calculated as $8.8 \pm 0.5 \text{ nmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ and $0.9 \pm 0.04 \text{ nmol}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, respectively. One contributing factor to the observed increase in selectivity was greater adsorption of PEI molecules. Notably, highly adsorbed PEI segments, characterized by a more hydrophobic, ethylene-rich backbone, lowered the water uptake value of CMV_PEI_5_0, causing reduced swelling. This increased adsorption with a more compact structure of PEI provided better surface coverage. Furthermore, an increase in the surface charge density of the membrane was observed. As a consequence, at a deposition pH of 5, a more synergistic effect of sieving and Donnan exclusion compared to the deposition case of pH 3 exerted a more effective influence against the transport of copper ions. Since copper ions are characterized by both larger size and higher valency, superior Ag^+/Cu^{2+} selectivity was achieved. With a further increase in deposition pH to 7, a slight decrease in the selectivity (14.5 ± 0.9) was observed. Despite greater adsorption at pH 7, fewer free positive charges were obtained on the membrane surface. In addition, the lower water uptake value of the CMV_PEI_7_0 compared to CMV_PEI_5_0 suggests more swelling and easier penetration of both ions, resulting in reduced Ag^+/Cu^{2+} selectivity.

3.5.2. Effect of ionic strength of PEI solutions

The ionic strength of the PEI solution was another decisive factor influencing monovalent selectivity and also altering the membrane surface properties. When salt was added to the PEI solution, the selectivity performance of the membranes enhanced compared to their salt-free cases, but the selectivity trend for the membranes with different deposition pH values remained consistent. The membranes modified by PEI at pH 3, 5, and 7 in the presence of salt improved the selectivity performances to 11.9 ± 0.3 , 20.2 ± 0.9 , and 17.1 ± 0.2 , respectively. Numerous reasons can enlighten these findings. As previously discussed, the active charges on PEI monomer are screened by small counter-ions of salt, causing the formation of lumpy and more compact PEI segments with a reduced radius of gyration [52]. Consequently, PEI segments with a smaller surface area per chain can deposit more on the membrane with the same surface area, enabling a higher density of PEI and improved surface coverage ([Scheme 2b](#)). Furthermore, the reduced charge density by the addition of salt further decreased the water uptake values, making the membranes less prone to swelling. Additionally, higher water contact angle values confirmed the more hydrophobic surface of the membranes modified in the presence of salt ions, impeding the transfer of copper ions more than silver ions. This distinction arises because copper ions have much higher charge density, enabling them to strongly associate with water clusters and making the destruction of the hydration shells more challenging compared to silver ions [66,67]. Conversely, silver ions, with an energy of hydration approximately five times lower, can more readily rearrange surrounding water molecules ([Table 3](#)). As a consequence, the difference in energy of hydration between the two ions represents its potential for selective recovery, called dielectric effect [68], in addition to the size and Donnan exclusion effects.

The highest monovalent selectivity was achieved at a deposition pH of 5 with 0.5 M NaCl (20.2 ± 1.0). It is also important to note that the selectivity performance of the PEI-modified membrane at pH 3 in the

presence of salt was surpassed by membranes deposited at pH 5 and 7 in the absence of salt and was similar to that of CSE-WS (12.2 ± 0.1). In conclusion, the selectivity performance across the membranes can be generalized as follows: $CMV_PEI_5_0.5 > CMV_PEI_7_0.5 > CMV_PEI_5_0 > CMV_PEI_7_0 > CSE-WS > CMV_PEI_3_0.5 > CMV_PEI_3_0$. From these results, it can be deduced that membranes modified in weakly acidic conditions with added salt yielded the highest monovalent selectivity due to greater adsorption with a packed and more hydrophobic structure. In contrast, acidic or neutral deposition conditions in the absence of salt either limited the adsorbed amount or the charge density of the modified layer.

The results suggest that fine-tuning a selective layer provides a straightforward and efficient method for synthesizing CEMs for selective monovalent/bivalent metal ion separation in electrodialysis. The observed selectivity among cations is influenced by electrostatic barriers, steric hindrance, and dielectric effects, all of which stem from differences in ion valency, size, and hydration energy in conjunction with the unique properties of the developed membranes.

3.6. Energy consumption

The energy consumption of the CEMs to separate silver from copper ions was calculated ([Fig. 10](#)). The spent energy per mole of copper ions for unmodified CMV was lower than that of PEI-modified membranes. The reason is that the CMV membrane is more permeable to copper ions, transporting more current supplied to the system, thereby requiring less energy input. The energy requirement per mole of silver ions, on the other hand, was found to be higher for the unmodified membrane. This result confirms the preference for the transport of copper ions, owing to their higher affinity than silver ions when interacting with the unmodified membrane. In the case of monovalent selective membranes, the needed energy to transport one mol of silver ions was much less compared to copper ions. Copper ions began to encounter more resistance in migration through the modified membranes due to the altered surface properties, which led to a decreased interaction between the copper ions and the membrane. The results suggest that the modified membranes with distinct surface properties such as charge density, adsorbed amount, thickness, and conformation have more implications for copper than silver permeation. In contrast, the spent energy to permeate per mole of silver ions was similar for each monovalent selective membrane. These findings can be related to an increased resistance toward the migration of copper ions, whose flux underwent a dramatic decrease, whereas the flux of silver ions did not change substantially, displaying a correlation between the energy consumption and ions' migration rates. [Figure S14](#) compares the current efficiency in electrodialysis when different sets of CEMs are used. The results reveal that the current efficiency doubled that of the unmodified membrane when PEI-modified membranes were used, demonstrating a significant enhancement in the transport of current by silver ions.

3.7. Effect of feed solution pH

During the treatment of the metal mixtures through the membranes in electrodialysis, the choice of the feed solution pH is critical. The solution pH influences the charge of the metal species providing either more metal ions or solid forms as a precipitate. Moreover, the protonation degree of the modified membranes is influenced by the feed pH due to the presence of pH-responsive groups of PEI segments on the membrane surface, which determines the type of interaction between metal ions and the membrane surface, affecting the overall efficiency.

A trace amount of $AgNO_3/Cu(NO_3)_2 \cdot 3H_2O$ mixture was added into the colorless PEI solution prepared in strongly ($pH < 3$) and weakly acidic media ($3 < pH < 6$), and the response of the PEI solution to the metal mixture was illustrated in [Figure S15a](#) with corresponding color changes and equations. When the metal mixture was added to weakly acidic PEI media, the solution turned to a blue color as a result of the

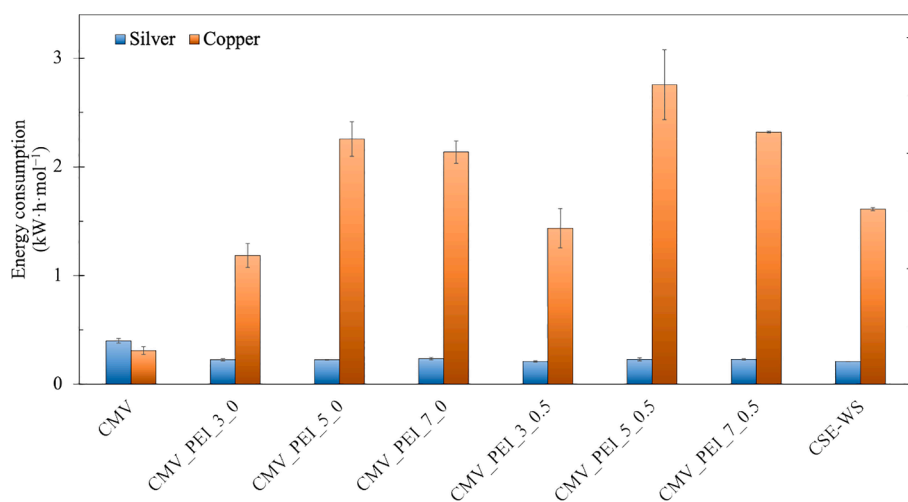


Fig. 10. The energy consumption of the commercial and PEI-modified CEMs.

chelation of copper ions with unprotonated amine groups [69,70]. It is essential to note that copper ions have a much higher coordination affinity for amine groups on PEI than silver ions [71]. The addition of the feed mixture to the strongly acidic solution of PEI did not cause a color change due to the ionization of unprotonated amines by protons, hampering the chelation of copper ions but inducing charge-charge repulsion [72].

The effect of the feed pH was also investigated through electro dialysis experiments. Figure S15b represents the surface of the unmodified and PEI-modified membranes subjected to the feed solution at the pH values of 2.3 or 5 for 2 h of electro dialysis. When the feed pH of the binary mixture was 5, the CMV membrane displayed a clean membrane surface, whereas the precipitation of the metal ions occurred on the PEI-modified membrane, which can be explained by the fact that unprotonated amine groups on PEI-modified membranes can make a complex with metal ions by chelating, causing metal precipitation on the membrane surface during electro dialysis. Lowering the feed pH to 2.3 induces the ionization of attached uncharged amines on the membrane surface, as proved by color intensity measurements. This, in turn, causes charge-charge interaction to be prevalent over chelation, impeding the metal ion from coordinating with the membrane surface. Meanwhile, as expected, the CMV membrane displayed a clean membrane surface regardless of the feed pH due to the lack of unshared electron pairs in its structure. Consequently, when unshared electron pairs of the atoms are present on the membrane surface, the adjustment of feed pH should be taken into consideration to ionize the functional groups so that possible metal precipitation can be prevented during the electro dialysis process.

3.8. Acid stability test

The chemical stability of the selected CMV_PEI_5_0 membrane was evaluated by immersing the modified membrane in an HNO₃ solution at pH 2.3 for 6 days, corresponding to the feed solution pH. As shown in Fig. 11, the flux of silver and copper ions remained unchanged after 6 days of membrane exposure to the HNO₃ solution, indicating consistent monovalent selectivity performance. The stability of the PEI-modified membrane can be attributed to the pH-responsive groups present in the PEI segments attached to the membrane surface. These groups exhibited increased protonation due to the interaction with hydrogen ions from the acid (HNO₃) at lower pH values, aligning well with color intensity measurement findings. As a result, an increased proportion of protonated groups led to more electrostatic attraction and stronger bonding of PEI segments to the membrane surface. These results suggest the potential of developed monovalent selective membranes, constructed through a single PEI layer assembly, to withstand harsh acidic industrial effluents for long-term operation.

4. Conclusions

The tailor-made monomolecular layer PEI-modified CEM with high Ag⁺/Cu²⁺ selectivity was developed, and the selective recovery of silver from copper ions using the developed CEM was demonstrated in a single-stage electro dialysis process. A monomolecular layer of PEI was deposited on the standard CMV membrane with fine-tuned morphology by adjusting deposition conditions. This alteration affected the adsorbed amount of PEI, charge density, and layer structure. Upon optimization of the deposition conditions, the PEI-modified membrane demonstrated notable efficacy in relation to metal selectivity, along with a robust resistance against acidic conditions.

The pH values in the PEI solution was one of the major factors for tailoring the final surface properties. Acidic PEI deposition (pH = 3) yielded low adsorption, while weakly acidic (pH = 5) or neutral (pH = 7) conditions increased adsorbed PEI (pH 7 > pH 5) and charge density (pH 5 > pH 7). Weakly acidic deposition also minimized membrane swelling, suggesting improved monovalent selectivity. The ionic strength of the PEI solution was another influential factor in altering surface properties. Adding salt to the PEI solution screened PEI monomer charges, increasing adsorbed PEI while reducing free positive charges on the membrane. The salt presence induced a compact, hydrophobic layer structure, enhancing selectivity compared to salt-free cases.

The choice of feed solution pH plays a critical role in preventing metal precipitation in the solution or on the membrane surface. At a feed

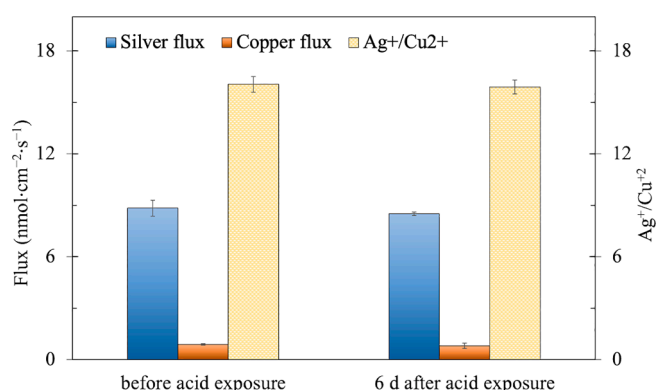


Fig. 11. The acid stability of the CMV_PEI_5_0 membrane.

pH of 5, PEI-modified membranes formed complexes between PEI and metal ions due to the presence of unprotonated nitrogen sites capable of chelating with copper ions. Conversely, an acidic feed pH (2.3) led to the protonation of attached PEI, effectively inhibiting metal precipitation. Additionally, the modified membrane maintained consistent performance even after 6 days in a strongly acidic HNO₃ solution. These results highlight the potential use of these membranes in harsh, acidic environments.

The findings suggest that electrodialysis utilizing functionalized IEMs has the potential for effective metal separation and recovery at a large scale, providing continuous operation for various metal effluents. Designing a tailored selective layer offers a simple and effective approach to creating monovalent selective membranes for metal ion separation in electrodialysis. Continuous research and development efforts are essential to unlock the potential of membrane-based technology in various specialized metal separation applications, including the separation of alkali metals sodium, potassium, and lithium, as well as precious metals from divalent metal impurities, all of which play a crucial role in the industrial circle, avoiding solid waste generation and using additional chemicals, thereby bringing in additional environmental advantages.

CRedit authorship contribution statement

Önder Tekinalp: Conceptualization, Methodology, Formal analysis, Validation, Investigation, Writing – original draft, Visualization. **Pauline Zimmermann:** Investigation, Writing – review & editing. **Simon Birger Byremo Solberg:** Investigation, 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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2023.147140>.

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