



Significantly enhanced dehalogenation selectivity in near-neutral zinc sulfate electrolytes by diffusion dialysis



Huan Cheng^{a,1}, Hui-Fang Xiao^{a,1}, Qing Chen^a, Xiu-Min Li^a, Wen-Meng Qin^a, Bao-Sheng Chen^b, Dong Xiao^b, Wei-Ming Zhang^{a,*}

^a College of Chemistry & Materials Engineering, Wenzhou University, Wenzhou 325000, PR China

^b Jingrun Envirotech Co., Ltd., Beijing 100085, PR China

ARTICLE INFO

Keywords:

Dechlorination
Permeability
Zinc sulfate electrolyte
Diffusion dialysis
Selective ion separation

ABSTRACT

For industries around the world, the hydrometallurgical roast–leach–electrowin process is the most common means of producing zinc metal. Dechlorination from the highly-concentrated zinc sulfate electrolyte is of vital importance to the zinc industry. In a recently published work, we innovatively employed diffusion dialysis (DD) to selectively remove Cl⁻ and F⁻ from a highly-acidic spent electrolyte, which extended the application of DD from acid recovery to selective ion separation. In the current paper, we greatly enhance the dechlorination selectivity by adjusting the acidity of feed electrolytes. The Cl⁻/SO₄²⁻ permeability increases from 2.56 to 42.8 when the acidity is reduced from 160 to 0 g/L as free H₂SO₄, and meanwhile the removal ratio of Cl⁻ impurity is basically retained (from 55.1% to 46.6%). The competitive permeation of different ions and the interplay between anions and cations are carefully investigated. It is believed that the distinct diffusivity of anions (Cl⁻, F⁻, HSO₄⁻ and SO₄²⁻) originates from their different hydrated sizes. This excellent selectivity observed here is unprecedented and has never been observed in any practical DD processes. It not only remarkably improves the cost-effectiveness of the dechlorination process in zinc production, but also puts forward a new possibility to regulate the permeabilities between ions with the same charge sign and provides new insights into the DD process in the selective ion separation.

1. Introduction

For industries around the world, most of the metallic zinc (~80%) is produced by the hydrometallurgical roast–leach–electrowin process. [1] Briefly, zinc, calcined from zinc blends, is dissolved in sulfuric acid and becomes a neutral ZnSO₄ electrolyte (pH ~5.0) in the leaching stage, finally producing Zn through the process of electrowinning. After a cycle, the spent electrolyte, containing sulfuric acid, a small amount of ZnSO₄ and residual impurities from the ores, will be sent back to the leaching section of the circuit. Carried out repeatedly, this process leads to an accumulation of impurities, which have undesired impacts on the process and its products. [1,2] For example, the Cl⁻ concentration should not exceed 500 mg/L in zinc electrolyte; otherwise it will corrode the Ag–Pb anodes and degrade the zinc product because of the increased Pb content. Therefore, the major issue facing hydrometallurgy is the purification of electrolytes, which ensures smooth electrowinning, high-purity cathode zinc products and low energy consumption.

In conventional practices, it is very difficult to get rid of the halide impurities (especially Cl⁻) from the electrolyte circuit. Up to now, numerous efforts have been made to tackle this challenge, but the outcomes have not been satisfactory. [3] Specifically, it includes: (1) Chlorides can be removed from electrolytes as precipitations, such as AgCl [4], Sn(OH)Cl [5], BOCl [6,7] and CuCl [8–12]. However, the operation costs are mostly extremely high because of cumbersome recycling procedures and unavoidable material losses [5,13,14]. Although the CuCl method is economically acceptable, it is still hard to implement because Cu²⁺ is more likely to form than Cu⁺ [8]. (2) The chlorides can be oxidized by ozone [15,16] or PbO₂ [17], and eliminated as Cl₂. Unfortunately, much more Mn²⁺ ions (10–20 times higher than Cl⁻) exist in the electrolytes [15,16], which will consume so many oxidants that the operation cost is unacceptable. (3) Ion exchange [18] and selective extraction [19,20] have also been utilized, but suffer from low efficiency, high zinc loss, and huge waste water emissions due to regeneration [18]. (4) Thermal methods are employed, since HCl and HF impurities are much more volatile than H₂SO₄ and sulfates. [21]

* Corresponding author.

E-mail address: weiming@iccas.ac.cn (W.-M. Zhang).

¹ These authors contribute equally to this work.

However, they are also unaffordable because of the high power consumption and costly corrosive-resistant equipment. (5) Conventional membrane processes, such as electrodialysis (ED), either with monovalent permselective ion exchange membranes (IEMs) [22] or with common IEMs assisted by nanofiltration (NF) membranes [23], have also been developed. However, as the concentration of salt solution increases, the permselectivities of these processes decrease dramatically and is barely effective in highly concentrated zinc electrolytes (~ 320 g/L for SO_4^{2-}). [24,25]

Very recently, we proposed a new approach to selectively remove the halide impurities from the spent zinc electrolyte directly by diffusion dialysis (DD). [3] In contrast to a conventional DD process, in which the acid is always reclaimed as a recovered pure chemical for reuse, the dilute H_2SO_4 here was instead treated as a waste stripping effluent. Halide impurities were removed from the electrolyte circuit successfully and cost-efficiently, and an unexpected enrichment of halide impurities was observed in the stripping stream. However, although the selectivity (~ 2.7 for Cl^- and ~ 1.5 for total F^- over total SO_4^{2-} at the optimal flow intensity) is relatively apparent in this new process, the loss of SO_4^{2-} is still tremendous in comparison with the removed Cl^- . For example, the composition of the waste DD effluent is 8.6×10^{-1} mol/L of H_2SO_4 and 8.8×10^{-3} mol/L of HCl at the optimal flow intensity. [3] As to how to further mitigate the sulfate loss is what should be considered as a follow-up improvement of this new approach. First, lower sulfate loss means better cost-effectiveness, because less H_2SO_4 makeup is needed in the hydrometallurgy process. Second, lower sulfate loss results in reduced waste chemical emission, which is favorable for the environment as well as waste disposal.

Since we have already started thinking outside the box, new possibilities emerge for the well-established DD process. As we have suggested, that the interesting permselectivity of anions (Cl^- over HSO_4^- in the spent electrolyte) originates from their different hydrated radii. [3] It should be enhanced if the HSO_4^- can be converted to SO_4^{2-} . Because of this, the SO_4^{2-} dianion has a higher charge number and electric field intensity, which will result in a stronger binding with H_2O molecules, a larger hydrated radius and consequently a lower diffusivity. It is noteworthy that this idea is impossible to implement within the framework of conventional DD process which is basically restricted to the acid recovery. Since the highly concentrated free acids must exist in the feed electrolyte stream before being recovered, it eliminates the existence of SO_4^{2-} (converted to HSO_4^- completely). In the current work, we attempt to boost the selectivity of removing halide impurities from the zinc electrolyte circuit by adjusting the acidity of feed electrolytes in DD process. This enhancement of permselectivity not only significantly improves the economics of the newly proposed strategy of electrolyte purification with DD, but also provides a possibility to regulate the permselectivity between ions with the same charge sign in IEMs.

2. Experimental

2.1. Materials

TWDDA AEM (Shandong Tianwei Membrane Technology Co., Ltd., China) was used in this study, and its detailed specifications can be found in our previous work. [3] All chemicals involved (Sinopharm Chemical Reagent Co., Ltd., China) were of analytical grade, and deionized water ($> 5 \text{ M}\Omega \text{ cm}$) was used during all DD tests. The real spent zinc electrolyte sample was provided by a major zinc producer in south China, and it was filtrated by $0.45 \mu\text{m}$ membranes to remove suspended solids before all tests. The neutral zinc electrolyte was prepared in our laboratory. Firstly, excess pure ZnO powders (AR, ca. 1.05:1) were added into the real spent zinc electrolyte under a mild stirring, and the reaction lasted overnight at room temperature ($25 \pm 0.5^\circ\text{C}$). Then the resulting solution was filtrated by $0.45 \mu\text{m}$ membranes to get a neutral zinc electrolyte (pH ~ 4.0). The electrolyte here is not completely neutral (pH ~ 5.0 for pure ZnSO_4 solution)

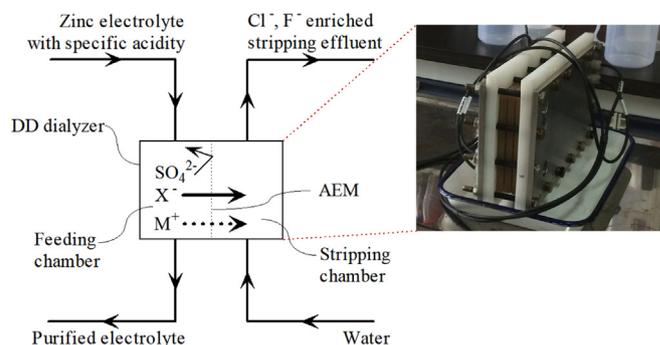


Fig. 1. Simplified process of the DD test in lab, and photograph of the dialyzer used in this study. X^- represents halide ions such as Cl^- and F^- , M^+ represents free H^+ and metallic cations such as Zn^{2+} , Mn^{2+} , Mg^{2+} , Na^+ and K^+ .

because a trace amount of H^+ still remains, however, which is not detectable by conventional methods such as titration (< 0.1 g/L as H_2SO_4 , in contrast to 160 g/L in the spent electrolyte). Therefore, this electrolyte is called the neutral electrolyte throughout this study.

2.2. Continuous DD tests with real electrolytes

The simplified scheme of the continuous DD test is presented in Fig. 1, and a photograph of the home-made dialyzer used in this study is also shown. The zinc electrolyte and pure water were pumped (BT-100 peristaltic pump) into the feed chamber and stripping chamber (i.e. recovery chamber in conventional DD) of the dialyzer, respectively. The dialyzer was equipped with also home-made tortuous path flow spacers (260 mm length \times 130 mm width \times 0.70 mm thickness, with an effective area of 187 cm^2). It consisted of three hydraulic stages with a 170-cm flow path, which simulated a full-scale commercial DD dialyzer (~ 160 cm). There were five spacers for both feed stream (zinc electrolyte) and stripping stream (deionized water) in each stage. The stack was equipped with 27 pieces of AEMs (TWDDA), two inter-stage PE sheets and 30 turbulence accelerating spacers, and the effective membrane area was 0.50 m^2 ($187 \text{ cm}^2 \times 27$ pcs). The detailed scheme and hydraulic characterization of the dialyzer has also been documented in our previous work. [3]

In the current study, the influence of the free acidity on the overall dechlorination performance was investigated intensively. Real zinc electrolytes with various free H_2SO_4 concentrations (0–160 g/L) were prepared in our lab by simply mixing a specific amount of spent electrolyte (high free H_2SO_4 , ~ 160 g/L) and neutral electrolyte (no free H_2SO_4 , 0 g/L). Subsequently, the resulted electrolytes were dechlorinated by DD (as shown in Fig. 1). The flow intensity of both feed and stripping streams was fixed at $4.0 \text{ L h}^{-1} \text{ m}^{-2}$ (corresponding flow rate of 2.0 L h^{-1}) at both inlets of the dialyzer in all tests, since it had been proven to be the optimum for cost-effectiveness in our previous work. [3] The inner volume was about 196 mL ($187 \text{ cm}^2 \times 0.7 \text{ mm} \times 15$ cells) for each chamber, and the resident time was about 6 min (flow velocity of 0.48 cm/s) for both feed and stripping streams. All tests were conducted at $25 \pm 0.5^\circ\text{C}$.

2.3. Analytical methods

The concentrations of Cl^- , total H^+ (including free H^+ and HSO_4^- , the end point of pH is ~ 4.50 in automatic titration), and total SO_4^{2-} (including SO_4^{2-} and HSO_4^-) ions were determined by potentiometric titration. The concentration of total F^- (including free F^- and HF) was measured by a fluoride ion selective electrode, and all metallic ions (including Zn^{2+} , Mg^{2+} , Mn^{2+} , Na^+ and K^+) were analyzed by ICP-OES (PerkinElmer Optima 8000). The detailed procedures of the analytical methods have also been described in our previous work. [3]

The removal ratio (also known as the recovery ratio for the

favorable mass transfer, or leakage ratio for the unfavorable mass transfer) of a species in a continuous DD process is calculated by the following formula: [3,26]

$$\eta = \frac{C_d^{out} Q_d^{out}}{C_f^{in} Q_f^{in}} = \frac{C_d^{out} Q_d^{out}}{C_f^{out} Q_f^{out} + C_d^{out} Q_d^{out}} \quad (1)$$

where C_f^{in} and C_f^{out} are the ion concentrations (mol/L) at the inlet and outlet of the feed stream, C_d^{out} is the ion concentration (mol/L) at the outlet of the stripping stream, Q_f^{in} and Q_f^{out} are the flow rates (L/h) at the inlet and outlet of the feed stream, Q_d^{out} is the flow rates (L/h) at the outlet of the stripping stream in the continuous DD process (shown in Fig. 1).

As we have discussed in our previous work, [3] the removal ratio in Eq. (1) is a practical indicator of the removal performance for a specific kind of ion in this continuous process. A high ratio signifies a priority to permeate across membranes, and vice versa. So, the relative ratio between the removal ratios of two ions can be a reasonable and straightforward gauge for the permselectivity in this study:

$$P_B^A = \frac{\eta_A}{\eta_B} \quad (2)$$

where P_B^A represents the permselectivity of ion A relative to ion B, η_A and η_B are the removal ratios of A and B, respectively.

3. Results and discussion

3.1. Electrolytes with various free acidities

Six different zinc electrolytes with various free H_2SO_4 acidities, which are 0, 2.0, 4.0, 8.0, 16.0 and 160 g/L as H_2SO_4 respectively, were prepared by mixing the corresponding amount of the spent zinc electrolyte (~160 g/L as free H_2SO_4) and the neutral zinc electrolyte (no free H_2SO_4). The actual chemical compositions of all resulted electrolytes were carefully analyzed by potentiometric titration, ion selective electrode and ICP-OES in our lab, and the detailed results are provided in Table S1 in Supporting information. The concentrations of all chemical species are almost equal except for the free acidity and Zn^{2+} concentration, so the basic facts of the compositions of all electrolytes can be summarized (basically averaged) and shown in Table 1. For the electrolyte with a higher Zn^{2+} concentration, the free acidity (as free H_2SO_4) is correspondingly lower, and the sum of H^+ and Zn^{2+} equivalent keeps constant (~5.0 N) due to the electrical neutrality.

After continuous running for ~2.0 h (only ~6 min resident time for the dialyzer) to make sure that the steady-state operation had already been achieved, we started collecting samples every 12.0 min at both outlets of feed and stripping streams. The precise flow rates of the two outlets are calculated by the sample volumes and sampling intervals, and the chemical compositions of all outlet samples are also analyzed.

Table 1
Detailed chemical compositions of zinc electrolytes with different acidities.

Ions	Concentrations	
	g/L	mol/L
Zn^{2+}	166→58 ^b	2.53→0.89 ^b
Mg^{2+}	27.6	1.14
Mn^{2+}	6.7	0.121
H^+ as H_2SO_4	0→160 ^a	0→1.63 ^a
Na^+	2.15	9.35×10^{-2}
K^+	0.661	1.69×10^{-2}
SO_4^{2-}	341	3.55
Cl^-	0.476	1.34×10^{-2}
F^-	0.122	6.43×10^{-3}

^a The acidity is presented as the concentration of H_2SO_4 in electrolytes.

^b The concentration of Zn^{2+} is higher for the electrolyte with lower acidity, and vice versa.

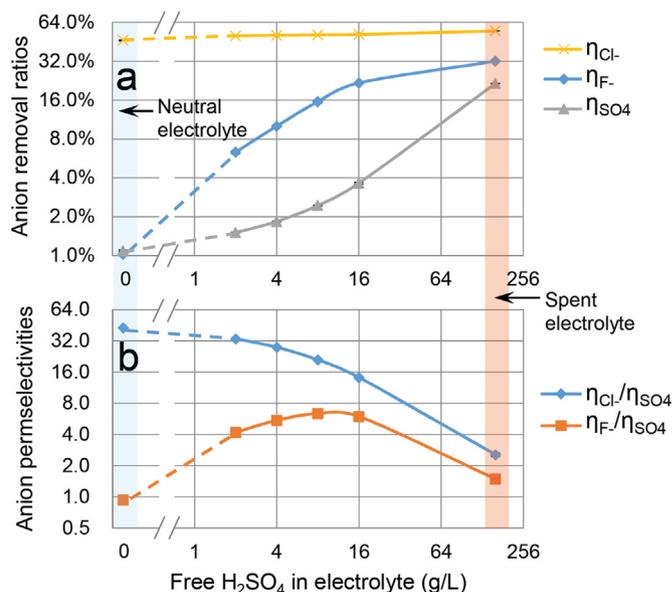


Fig. 2. Competitive diffusions of anions across the TWDDA membrane in different zinc electrolytes with varied free acidities. Semi-transparent rectangles are used to mark the zones of the neutral and spent electrolytes. (a) The removal ratios of all anions, including Cl^- , total F^- and total SO_4^{2-} ions. (b) The permselectivity of Cl^- and total F^- ions respectively, over total SO_4^{2-} ions.

Typically, five samples were collected in all tests, and at least the last three samples were analyzed. The result shows that both flow rates and chemical compositions of these three samples are all nearly identical, and the averages of the detailed compositions and outlet flow rates are also provided in Table S1 in Supporting information. By comparing the data of inlet and outlet, the flow rates (also volumes) increase for the zinc electrolyte stream while decrease for the water stream in all DD tests, and these changes are more obvious for the electrolytes with lower acidities.

3.2. Competitive permeation of anions

As mentioned above, the flow rates and concentrations of anions in both outlet streams are listed in Table S1, and the removal ratios of anions can be calculated by these data according to Eq. (1) and plotted vs. the free acidity (on a logarithmic scale) of test electrolytes in Fig. 2a. It should be noted that “zero” (the free acidity of the neutral electrolyte) cannot be plotted in the logarithmic manner, so it is presented in an extra coordinate system (linear scale) aside the logarithmic plot, separated by double slashes, for a convenient comparison. The dashed lines between the two different coordinate systems serve merely to visually distinguish them in this figure. It was observed that both flow rates and concentrations of these samples are all nearly identical. This was also true for the removal ratios. All data here are obtained from the average of 3 individual samples, and error bars are also included on these plots. However, the error bars here are too small to be visible on the plots, especially in a logarithm manner.

When the free acidity of electrolyte is reduced from 160 to 0 g/L as H_2SO_4 , the removal ratio of Cl^- (η_{Cl^-}) basically keeps stable and slightly decreases from 55.1% to 46.6%. However, for the total F^- and total SO_4^{2-} ions, the changes are much more significant, which are from 32.1% to 1.0% and 21.5% to 1.1%, respectively. The data indicate that the free acidity of the zinc electrolyte has a minor impact on the permeation of Cl^- impurities across the TWDDA membrane, but can greatly mitigate the loss of SO_4^{2-} ions.

Since the ultimate goal of the current work is to remove Cl^- from the zinc sulfate electrolyte, the permeation of Cl^- in DD dialyzer is favorable, while that of SO_4^{2-} is unfavorable. The permselectivity of anion

impurities over total SO_4^{2-} are reasonable indicators to evaluate the purification performance of DD process, which are calculated by Eq. (2) and plotted in Fig. 2b. Inspiringly, $P_{\text{SO}_4^{\text{Cl}}}$ increases from 2.56 to 42.8 as the free acidity decreases from 160 to 0 g/L as H_2SO_4 . For the total F^- ions, the situation is more complicated. Although η_{F^-} decreases when the acidity is reduced, which is seemingly similar to that of total SO_4^{2-} ions, their variation patterns are distinctly different. As shown in Fig. 2a, η_{F^-} drops sharply at low acidity and mildly at high acidity, while η_{SO_4} is the opposite, and the different patterns cause a non-monotonous change of $P_{\text{SO}_4^{\text{F}}}$. It rises from 1.49 (160 g/L acidity) to 6.38 (8 g/L acidity), and then tails off to 0.94 (0 g/L acidity). In Fig. 2, the performance benchmark of the same membrane used in our previous work with the spent electrolyte (160 g/L acidity) has been marked with a red rectangle area in both panels. [3] It's shown clearly that by controlling the electrolyte acidity, $P_{\text{SO}_4^{\text{Cl}}}$ and $P_{\text{SO}_4^{\text{F}}}$ increase to 16.7 times and 4.28 times our previous data, respectively, which means a great performance improvement.

In addition, η_{Cl^-} is moderate in all test electrolytes (55.1–46.6%, in Fig. 2a), which can be interpreted that the new strategy can only remove a part of Cl^- from the electrolyte in one cycle. It may be not cost efficient to get rid of all Cl^- (ca. > 95%) this way (by a multi-stage running), but quite appropriate and effective to keep the concentration at a low level and avoid a buildup, which is exactly the case for the dechlorination in the zinc industry [1,2]. Technically, a removal ratio of ~50% is able to completely meet the dechlorination demands. Furthermore, η_{Cl^-} remains basically stable even when the free acidity of the electrolyte decreases greatly, which means that the dechlorination capacity of the DD dialyzer can also keep stable in the variations of free acidity. So, removing the Cl^- impurity by DD from the near-neutral zinc electrolyte is feasible and effective just as we have accomplished from the highly acidic spent electrolyte, [3] and it is even better at reducing sulfate loss due to the significant enhancement of the permselectivity.

3.3. Competitive permeation of cations

Similarly, the removal ratios of all cations are also calculated by Eq. (1) and plotted in Fig. 3a, according to the flow rates and the cation concentrations of both outlet streams (also listed in Table S1). In

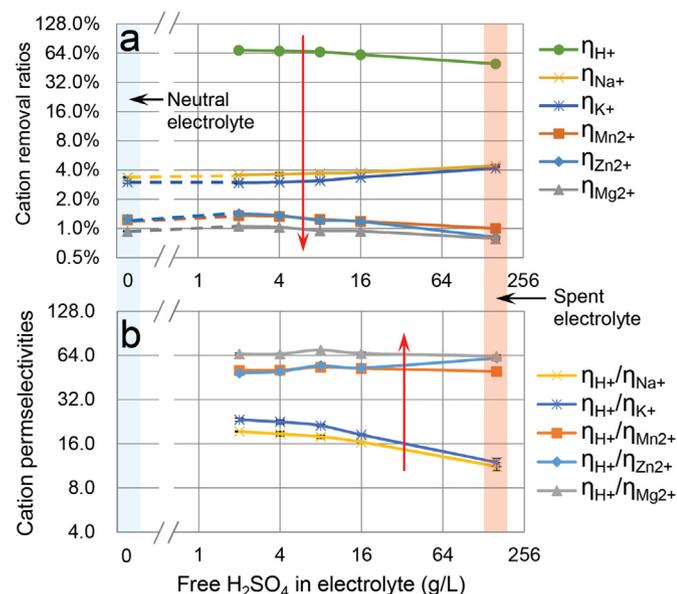


Fig. 3. The competitive leakages of cations across the TWDDA membrane in the different zinc electrolytes with varied free acidities. (a) The removal ratios of all cations, including total H^+ , Na^+ , K^+ , Mn^{2+} , Zn^{2+} and Mg^{2+} ions. (b) The permselectivity of total H^+ ions over Na^+ , K^+ , Mn^{2+} , Zn^{2+} and Mg^{2+} ions respectively.

addition, the data here are also obtained from the average of three individual samples with high reproducibility, so the error bars are barely visible. In general, each of them is roughly stable as the free acidity varies. It is not hard to notice that η_{H^+} is the highest one, which increases from 49.6% to 68.7% when the free acidity is reduced from 160 to 2.0 g/L as H_2SO_4 . The removal ratios of divalent cations (Mn^{2+} , Zn^{2+} and Mg^{2+}) are all very low (~1%), and the trends are also quite similar. As the free acidity descends, their diffusion increases in the acidity range from 160 to 2.0 g/L, while slightly decreasing at 0 g/L (neutral electrolyte) because their permeation across membranes is retarded by the very low overall diffusivity of anions (see Fig. 2a). For example, $\eta_{\text{Zn}^{2+}}$ goes up from 0.81% (160 g/L acidity) to 1.42% (2.0 g/L acidity), and lastly falls to 1.25% (0 g/L acidity). The removal ratios of monovalent metallic cations (Na^+ and K^+ , ~4%) are significantly higher than those of divalent cations. Meanwhile the variation tendencies are also different, which slightly decrease with the reduced free acidity. For example, η_{Na^+} steadily drops from 4.44% to 3.36%, when the free acidity is adjusted from 160 to 0 g/L as H_2SO_4 .

The high removal ratio of total H^+ results in remarkable H^+ selectivities over metallic cations, which are also calculated by Eq. (2) and plotted in Fig. 3b. Specifically, the permselectivities of total H^+ over divalent cations are as high as 50–70, and they are not obviously affected by the free acidities of test electrolytes. The permselectivities of total H^+ over monovalent cations are also good (although greatly lower than H^+ /divalent cations), which are about 11–20. In addition, a legible uptrend can be observed for the H^+/Na^+ and H^+/K^+ permselectivities in Fig. 3b, as the free acidities decrease from 160 to 2.0 g/L as H_2SO_4 .

The interplay between cations and anions is mainly rooted in the electrostatic interaction and it will influence the behaviors of ions permeability. Because the electric neutrality must be strictly maintained in the solution and membrane phase during the DD process, [27] the ion permeation will be accelerated when the counter ion has a higher diffusivity, and vice versa. [3,27] As mentioned before, the basic chemical compositions of the test zinc electrolytes are stable, except for the free acidity and Zn^{2+} concentration. The higher the free acidity is, the lower the Zn^{2+} concentration will be. H^+ has the highest mobility in aqueous environments because of the Grotthuss mechanism. [28] Thus, the overall cation diffusivity is larger for the electrolyte with a higher free acidity, and it gives rise to acceleration for anions and retardation for other cations, which has been proven by the experimental data. As the free acidity increases from 2 to 160 g/L, the apparent diffusivity increases for Cl^- (50.4–55.1%) in Fig. 2a, and decreases for total H^+ ions (68.7–49.6%) and divalent cations (1.36–1.00% for $\eta_{\text{Mn}^{2+}}$, 1.42–0.81% for $\eta_{\text{Zn}^{2+}}$ and 1.05–0.78% for $\eta_{\text{Mg}^{2+}}$) in Fig. 3a.

Different from that of divalent cations and free H^+ ions, the removal ratio of monovalent metallic cations (Na^+ and K^+) exhibits a puzzling upward trend as the free acidity increases. Because the factors involved in this multi-component permeation process are complicated, comprehensive theoretical calculations may be needed to determine the exact cause. Herein a reasonable speculation based on experimental data is proposed preliminarily. Briefly, it is probably also the result of the interplay between anions and cations, which ensures electric neutrality. Besides the influence of H^+ permeation retarding the transport of cations mentioned above, the anion permeation also accelerates the transport of cations. Namely the acceleration/retardation effects between cations and anions are bidirectional, and the overall effects may be different, depending on the properties of specific cations. Owing to the small hydration sizes, the permeation rates of Na^+ and K^+ are much higher than those of divalent cations (Mn^{2+} , Zn^{2+} and Mg^{2+}), resulting in higher removal ratios in Fig. 3a and lower H^+/Na^+ and H^+/K^+ selectivities in Fig. 3b. As the free acidity of electrolytes increases, the anion flux increases rapidly because the divalent SO_4^{2-} (low diffusivity) converts to monovalent HSO_4^- (high diffusivity), which enhances the permeation of Na^+ and K^+ ions more obviously and causes the puzzling response.

3.4. Potential mechanism for the enhancement of anion permselectivity

As shown in Fig. 2a, η_{Cl^-} is almost stable in zinc electrolytes of different acidities, and only a slight decrease is observed (from 55.1% to 46.6%) when the acidity is reduced from 160 to 0 g/L as H_2SO_4 . It consists well with the fact that HCl is a very strong acid ($\text{pK}_a -6.3$) and all chlorides exist as dissociated Cl^- ions in all electrolytes. The minor degradation of η_{Cl^-} is caused by the electrostatic interaction between cations and anions, which was already discussed in Section 3.3.

In comparison with η_{Cl^-} , η_{F^-} is much lower in all the test electrolytes (Fig. 2a), which can also be explained by the difference in size of the hydrated ions. Although with the same charge, the bare F^- is 25% smaller than the bare Cl^- , so the surface charge density of F^- is higher. Consequently, its hydration is stronger and the size is bigger, [29,30] which results in a lower diffusivity (i.e. a lower removal ratio) especially in the electrolyte with a small free acidity. When the acidity is reduced from 160 to 0 g/L as free H_2SO_4 , η_{F^-} decreases rapidly from 32.1% to 1.0%. This downtrend is quite different from that of Cl^- , probably due to the relatively weak acidity of HF ($\text{pK}_a 3.17$). In other words, even in the relatively low acidic electrolyte, the fluorine element may still be present in the form of the neutral HF molecule, which can permeate through the AEMs more easily because it has no electrostatic interaction with the positive-charged membrane matrix. The experimental data confirm this point of view. The removal ratio of total F^- ions falls slowly in quite a wide range (160→8 g/L) and speeds up in a narrower range of low acidity (8→0 g/L).

As shown in Fig. 2a, $\eta_{\text{SO}_4^{2-}}$ drops faster in the high acidity range. The pK_a of HSO_4^- is 1.99, distinctly lower than that of HF ($\text{pK}_a 3.17$), which means a stronger acidity than HF. Both removal ratios of total F^- (1.0%) and total SO_4^{2-} (1.09%) are very low in the neutral electrolyte (0 g/L, $\text{pH} \sim 4$), because F^- exist mostly as F^- ions and nearly all S exist as SO_4^{2-} dianions. The SO_4^{2-} dianion has a higher charge number and electric field intensity, which will result in a stronger binding with H_2O , a larger hydrated radius and consequently a very low diffusivity. As the acidity of electrolyte increases (0→8 g/L), F^- ions have a priority to combine with the free H^+ to get neutral HF molecules when compared with SO_4^{2-} dianions (potential to get HSO_4^-), which increases η_{F^-} more significantly than $\eta_{\text{SO}_4^{2-}}$. When the acidity of electrolyte becomes relatively high (8→160 g/L), most F^- have already existed as HF, and then the increase of η_{F^-} slows down. Meanwhile, without the competition of F^- , SO_4^{2-} dianions readily combine with the free H^+ to form HSO_4^- which is easy to permeate through the membrane. Finally, the $\eta_{\text{SO}_4^{2-}}$ rises faster in the high acidity range, as the free acidity of electrolyte increases. As a result, the different change patterns of η_{F^-} and $\eta_{\text{SO}_4^{2-}}$ cause a non-monotonical change of $P_{\text{SO}_4^{2-}}^{\text{F}^-}$ with the acidity (Fig. 2b). In contrast, the trend of $P_{\text{SO}_4^{2-}}^{\text{Cl}^-}$ is much more straightforward. It increases monotonically from 2.56 to 42.8, which is the result of a combination of stable η_{Cl^-} and descending $\eta_{\text{SO}_4^{2-}}$ as the acidity is reduced from 160 to 0 g/L.

In addition, the higher permeation rates of Na^+ and K^+ than those of divalent cations (Mn^{2+} , Zn^{2+} and Mg^{2+}) in Fig. 3a further supports the above mechanism. The surface charge density of divalent cations is significantly higher than monovalent cations, which will result in a stronger binding with H_2O , a larger size of hydrated ion, and then a lower diffusivity. The corresponding permselectivity of monovalent cations (Na^+ and K^+) vs. divalent cations (Mn^{2+} , Zn^{2+} and Mg^{2+}) is about 4.0. The results here clearly indicate that, at least in the current situation, the conventional IEMs show permselectivities between ions with the same charge sign (between not only different counter-ions but also different co-ions).

3.5. Practical considerations

3.5.1. Electrolyte acidity adjustment

The basic diagram of the hydrometallurgical process in the zinc industry and the integration with DD dechlorination are illustrated in

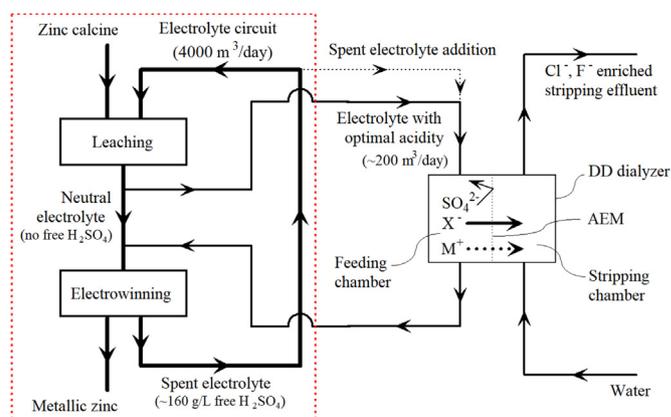


Fig. 4. An improved DD dechlorination process to enhance the permselectivity of Cl^- over total SO_4^{2-} by involving the feed electrolyte with an optimal acidity. The original hydrometallurgy process for zinc production is also marked with a dashed box. X^- represents halide ions such as Cl^- and F^- ; M^+ represents free H^+ and metallic cations such as Zn^{2+} , Mn^{2+} , Mg^{2+} , Na^+ and K^+ .

Fig. 4. First, the zinc calcine is leached with H_2SO_4 to obtain a neutral zinc electrolyte. Then, the neutral electrolyte is sent to a tank house to produce metallic zinc and regenerate H_2SO_4 (i.e. spent electrolyte) by electrolysis. Because the sulfate electrolyte circulates in a closed loop, it is essential to avoid the build-up of chloride impurities. Based on the above results and discussion, a potential dechlorination strategy from the zinc electrolyte with the optimal free acidity (near-neutral) has also been shown in the right part of Fig. 4. Basically, the halides are removed from the near-neutral electrolyte by involving a partial bypass circulation through the DD dialyzer. In order to adjust the free acidity of the feed electrolyte in the dialyzer, a small amount of the spent electrolyte was added into the feed stream of DD. Since the portion of the bypass circulation (< 5%) and the dosage of free acidity are low, [3] the main chemical compositions such as Zn^{2+} and SO_4^{2-} are virtually unchanged in the main zinc electrolyte circuit (marked in the dashed red box in Fig. 4). According to this scheme, the integration of DD is able to remove halides efficiently (especially for Cl^- , which hasn't been achieved satisfactorily by other methods) and minimize the impact on the hydrometallurgical process.

In addition, although the zinc in calcines is mostly ZnO , there are also other forms, such as zinc ferrite and zinc silicate. [2] In order to maximize the utilization of zinc resources, different leaching regimes are commonly employed, such as neutral leaching, weak acid leaching, hot acid leaching and strong acid leaching, which are applied in a multi-stage countercurrent format. [2] Therefore, the zinc electrolytes with various free acidities between 160 g/L (fresh spent electrolyte) and 0 g/L (neutral electrolyte) have already been available in the zinc industry, as the free acidity of the spent electrolyte decreases successively in the consecutive leaching process. Consequently, we can directly obtain zinc electrolytes with a certain suitable free acidity for the DD purification without extra costs.

3.5.2. Volume expansion of the electrolyte circuit

Considered practically, it is known that the issue of volume expansion is a major drawback of the DD process, especially in a closed-loop system. In this work, it's composed of the water osmosis in the dialyzer and the concentrated H_2SO_4 makeup (to balance the sulfate loss), which are calculated and plotted in Fig. 5a. Because the ion concentration in the feed zinc electrolyte is extremely high (> 7 equivalent/L), the water migration from the stripping chamber (pure water side) to the feed chamber is severe due to water osmosis, resulting in a volume expansion of the feed solution. Based on the data of lab-scale continuous DD tests, the amount of water osmosis in a full-scale plant can be reasonably estimated by the increase of electrolyte

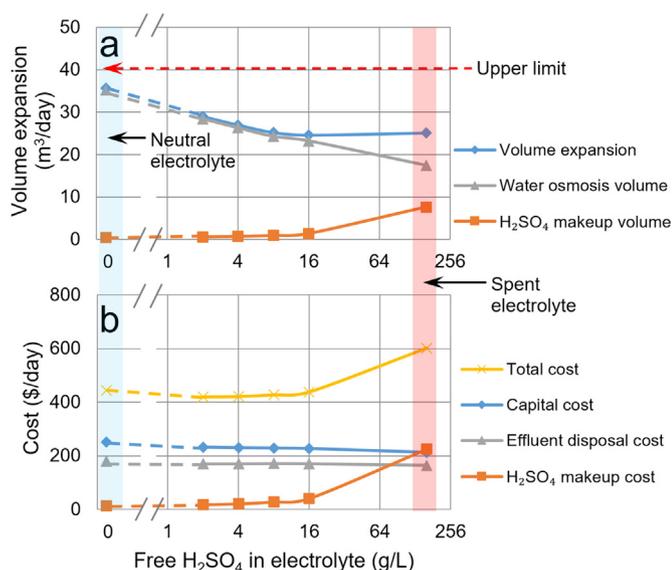


Fig. 5. The detailed volume expansion (a) and cost estimation (b) of the dechlorination process by DD for different zinc electrolytes with varied free acidities.

flow rate as well as the scale-up factor needed by the plant. The detailed procedure for the calculation of water osmosis is provided in Table S2 in Supporting information, and the results are shown in Fig. 5a. The water osmosis volume is distinctly negatively correlated with the free acidity of electrolyte, which is 35.2 and 17.5 m³/day for the neutral electrolyte and spent electrolyte, respectively. This experimental phenomenon is fully ascribed to the variation of electrolyte compositions. On the one hand, as Zn²⁺ are partially substituted by H⁺ (free acidity increases), the total ion concentration of the electrolyte decreases because H⁺ associates with SO₄²⁻ in the electrolyte to form HSO₄⁻ (number of ions decreases). Therefore, the total ion concentration is high for the feed electrolyte with a low free acidity, which gives rise to a high water osmosis. On the other hand, the flux of solutes (migration of ions, opposite direction to the water osmosis) from the feed to the stripping stream decreases significantly when the free acidity is reduced (see the removal ratio of total SO₄²⁻ in Fig. 2a), because the main chemical composition of the stripping effluent is H₂SO₄ at the outlet, especially for the electrolyte with a high free acidity. Since all ions are hydrated with plenty of water molecules, the water transport associated with the ion flux (opposite to the water osmosis) is more significant for the electrolytes with high free acidity, which abates the net water osmosis more and finally a decreasing monotonic plot is apparent.

The volume of H₂SO₄ makeup can be calculated based on the loss of total sulfate in DD purification, and plotted in Fig. 5a as well. It decreases tremendously with the reduced free acidity, which is 7.64 and 0.46 m³/day for the spent and the neutral electrolyte, respectively. The root cause of this improvement is the enhanced Cl⁻/SO₄²⁻ permselectivity (see Fig. 2b for details). The higher the permselectivity is, the less the loss of the total sulfate will be, when a fixed amount of Cl⁻ impurity is removed from the electrolyte circuit. The total volume expansion (water osmosis + H₂SO₄ makeup) of the zinc electrolyte in a full-scale plant is also plotted in Fig. 5a. The volume of the feed electrolyte expands considerably after the DD process, which may lead to unexpected failures. Fortunately, the electrolyte circuit in hydrometallurgy (the thickest loop in Fig. 4) can tolerate a certain amount of volume expansion in the industry, because the electrolyte loses some water during both leaching (especially in hot acid leaching and strong acid leaching, as high as 90 °C) [2] and electrowinning processes [1] due to water evaporation. The maximum acceptable volume of expansion, marked with a red dashed line in Fig. 5a, is ~40 m³/day (~1% × 4000 m³/day, the latter is the total amount of electrolyte circulation in

hydrometallurgy) [3] in the zinc plant which provides us with the zinc electrolyte samples. Although the water osmosis is serious in the DD dialyzer, fortunately only a very small portion of the electrolyte needs to be processed (~200 m³/day in 4000 m³/day, shown in Fig. 4). As a result, the total volume expansion of electrolytes caused by DD is totally acceptable in this study, even for the neutral electrolyte (35.2 m³/day), which suffers from water osmosis most, still below the upper limit (40 m³/day).

3.5.3. Overall cost analysis

Detailed procedures of the cost estimation of the selective dechlorination by DD have already been discussed in our previous work, and the total cost is composed of capital cost (DD dialyzer, etc.), disposal cost of stripping effluent, and chemical cost for H₂SO₄ makeup. [3] The procedures and parameters of the cost estimation for electrolytes with different free acidities are also provided in Table S2 in Supporting information, and the corresponding results are plotted in Fig. 5b. Since η_{Cl^-} decreases slightly with the reduced free acidity (Fig. 2a), a slightly larger DD dialyzer is needed. Consequently, the capital cost goes up correspondingly from \$212.7/day to \$251.5/day, as the free acidity decreases from 160 to 0 g/L as H₂SO₄. The disposal cost of the stripping effluent is quite stable (~\$170/day) for all electrolytes, which is a compromise of two opposite effects. On the one hand, η_{Cl^-} becomes lower as the free acidity decreases, so a higher amount of feed electrolyte needs to be treated by the DD bypass. Likewise, the amount of water needed in the stripping stream also increases (the flow rate of the feed and stripping stream is equal), which raises the stripping effluent as well as the disposal cost. On the other hand, the water transfer inside the dialyzer (i.e. water osmosis) increases when the free acidity is reduced as discussed in 3.5.2, which decreases the outlet flow rate of stripping stream and the disposal cost. The chemical cost of H₂SO₄ makeup drops rapidly from \$224.8/day to \$13.5/day, as the free acidity decreases from 160 to 0 g/L as H₂SO₄. Finally, the total costs of different electrolytes can be readily summed up by the above three portions, and the results are also plotted in Fig. 5b. The optimal free acidity is 2.0 g/L, and the lowest overall cost is \$419.8/day, which is significantly lower than that of the spent electrolyte in our previous work [3].

3.5.4. Waste effluent managements

As shown in Table S2 and Fig. 5b, the disposal costs of DD stripping effluents are nearly constant (~170 \$/day) for all electrolytes. The detailed chemical compositions of these waste effluents are also provided in Table S1. The concentration of Cl⁻ is almost unchanged in all effluents (~8 × 10⁻³ mol/L). However, the concentration of total SO₄²⁻ ions decrease rapidly (from 8.7 × 10⁻¹ mol/L to 4.6 × 10⁻² mol/L) as the free acidity decreases, which is caused by the significantly enhanced permselectivity of Cl⁻/SO₄²⁻. Since all effluents are dominated by total SO₄²⁻ ions (shown in Table S1), the total ion concentration also decrease as the free acidity decreases. For example, the total ion concentration of the stripping effluent is about ~0.90 mol/L and ~0.05 mol/L for the spent electrolyte (160 g/L acidity) and the neutral electrolyte (0 g/L acidity), respectively. It is very important to dispose of this effluent properly because of its high corrosivity and large volume. Since treating dilute effluents by common disposal methods is much easier in sewage treatment plants, the selective dechlorination from near-neutral electrolytes may facilitate the disposal of DD stripping effluent and further reduce the process cost in Fig. 5b. In addition, conventional membrane technologies can also be used to treat this effluent, and the benefits are twofold. Firstly, the volume of the effluent can be greatly reduced, which minimizes disposal costs as well as potential environmental impacts. Secondly, the recovered clean water is an ideal replenishment to the fresh stripping stream, which minimizes the total water consumption during the DD purification.

4. Conclusions

In this work, the selective dechlorination from the zinc electrolyte is significantly enhanced by adjusting its acidity. The permselectivity of Cl^- over total sulfate increases from 2.6 to 42.8, and the permselectivity of total F^- over total sulfate increases from 1.5 to 6.4, when the free acidity of the zinc electrolyte is optimized. Additionally, the transport of Cl^- across the membrane is maintained while the transport of total sulfate ions is greatly restrained as the free acidity decreases, which ensures high removal ratios of halide impurities as well as an extremely low loss of sulfate ions. The removal ratio is as high as 50% for Cl^- , while the loss ratios of zinc and sulfate are as low as 1.4% and 1.5%, respectively. The enhanced permselectivity enables the dechlorination more efficiently, which is helpful to minimize the stripping effluent (both volume and concentration), as well as the total water consumption in the DD process. The selectivity achieved here is unprecedented and has never been observed in the practical DD process with conventional AEMs, and it is possible to be unveiled only after breaking the think set of acid recovery. The excellent performance has not yet been achieved by other competitive methods (such as nanofiltration), because of the complexity and extremely high concentration of the zinc electrolyte solutions. It adds some original understanding to the selective ion separation of the well-established DD process and is likely to become its new growth point and future direction besides acid (or alkali) recovery.

Acknowledgements

The authors are grateful for financial support by the National Natural Science Foundation of China (21673159, 21203139 and 21003097).

Appendix A. Supporting information

Supplementary data associated with this article (Table S1 and S2) can be found in the online version at <http://dx.doi.org/10.1016/j.memsci.2018.05.053>.

References

- [1] B. Schwab, A. Ruh, J. Manthey, M. Drosik, Zinc, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
- [2] R.J. Sinclair, The Extractive Metallurgy of Zinc, The Australasian Institute of Mining and Metallurgy, Carlton, Victoria, 2005, p. 57.
- [3] H.-F. Xiao, Q. Chen, H. Cheng, X.-M. Li, W.-M. Qin, B.-S. Chen, D. Xiao, W.-M. Zhang, Selective removal of halides from spent zinc sulfate electrolyte by diffusion dialysis, *J. Membr. Sci.* 537 (2017) 111–118.
- [4] K.-Q. Yang, J.-W. Zheng, Process for removing chloride from zinc electrolytic solution by using silver hydroxide, CN Patent 1936036A, Mar. 28, 2007.
- [5] A.-H. Shi, R. Chen, W.-B. Yan, F. Gao, Method for removing chlorine from zinc or manganese electrolyte through using Sn (II) compound, CN Patent 102851503A, Jan. 2, 2013.
- [6] W.-H. Wu, J.-B. Liu, S.-Y. Tian, Z.-J. Wang, Z.-F. Su, Removal of chloride from zinc electrolyte with Bi_2O_3 , *Hydrometall. China* 33 (2014) 480–482.
- [7] Z.-M. Feng, S.-M. Ning, W.-J. Wang, Z.-H. She, H.-Q. Wan, J.-H. Wu, Dechlorination of zinc sulfate solution by bismuth oxide, *Min. Metall. Eng.* 35 (2015) 63–66.
- [8] F.J.J. Bodson, Process for the elimination of chloride from zinc sulphate solutions, US Patent 4005174, Jan. 25, 1977.
- [9] J.-P. Feng, G.-Q. Wu, Z.-Y. Zhou, Method for circularly removing chlorine in zinc sulphate solution by copper slag, CN Patent 101633982A, Jan. 27, 2010.
- [10] L.-Q. Wei, T.-L. Guo, M.-H. Wang, H.-G. Wang, Y.-Q. Cheng, Method for removing chlorine in zinc sulfate solution with high chlorine content, CN Patent 102796869 A, Nov. 28, 2012.
- [11] J.-H. Zhang, S.-K. Wang, Method for circularly removing impurity chlorine in zinc sulfate solution by using cuprous salt, CN Patent 102732725B, Jun. 19, 2013.
- [12] S.-Y. Wu, D.-C. Zhang, L.-W. Xiao, Method for removing fluorine and chlorine in zinc sulfate solution, CN Patent 105112660A, Dec. 2, 2015.
- [13] Q.-Z. Fei, W.-D. Liu, Improving of COD determination method and the recovery of silver, *Environ. Monit. China* 20 (2004) 23–24.
- [14] W.-H. Wu, J.-B. Liu, S.-Y. Tian, Z.-J. Wang, Z.-F. Su, Research of regeneration and recycle use of BiOCl in chlorine removal slag of zinc electrolyte, *China Nonferrous Metall.* 0 (2015) 71–73.
- [15] W. Liu, R. Zhang, Z. Liu, C. Li, Removal of chloride from simulated zinc sulfate electrolyte by ozone oxidation, *Hydrometallurgy* 160 (2016) 147–151.
- [16] G.L. Bolton, V.B. Sefton, N. Zubryckij, Removal of manganese and chloride ions from aqueous acidic zinc sulphate solutions, US Patent 4379037, Apr. 5, 1983.
- [17] G.-F. Yang, F.-R. Zhao, Q. Wang, Electrolytic Zinc waste a sulfated dechlorination process, CN Patent 103668324B, Jun. 29, 2016.
- [18] Z.-H. Song, Fluorine and chlorine removal process for zinc metallurgy industrialization ion exchange process with wet-process, CN Patent 101492772A, Jul. 29, 2009.
- [19] X.-D. Liu, J.-R. Qiang, Production process for isolating fluorine and chlorine by acid extraction during electrolytic zinc production, CN Patent 101886170B, May 30, 2012.
- [20] X.-Z. Tong, C.-L. Li, H.-X. Wang, Activation extraction separation method for fluorine and chloride ions in zinc sulfate, CN Patent 103451449B, Jul. 2, 2014.
- [21] S.P. Fugleberg, J.I. Poijarvi, Hydrometallurgical method for treating valuable metal raw materials containing chlorides and fluorides, US Patent 4698139, 1987.
- [22] D.L. Ball, D.A.D. Boateng, Method for removal of monovalent ions from ZnSO_4 electrolyte by electrodialysis, US Patent 4715939, Dec. 29, 1987.
- [23] J. Wu, Dechlorination method of zinc sulfate solution, CN Patent 103572051A, Feb. 12, 2014.
- [24] T. Sata, Ion Exchange Membranes: Preparation, Characterization, Modification And Application, Royal Society of Chemistry, Cambridge, 2004.
- [25] R.W. Baker, Membrane Technology and Applications, John Wiley & Sons Ltd, Chichester, 2004, pp. 209–210.
- [26] 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.
- [27] Y. Tanaka, Ion Exchange Membranes: Fundamentals and Applications, 2nd ed., Elsevier, Amsterdam, 2015, pp. 38–39.
- [28] N. Agmon, The Grotthuss mechanism, *Chem. Phys. Lett.* 244 (1995) 456–462.
- [29] Y.-L.S. Tse, H.N. Sarode, G.E. Lindberg, T.A. Witten, Y. Yang, A.M. Herring, G.A. Voth, Chloride enhances fluoride mobility in anion exchange membrane/polycationic systems, *J. Phys. Chem. C* 118 (2014) 845–853.
- [30] Y.-L.S. Tse, G.A. Voth, T.A. Witten, Ion mixing, hydration, and transport in aqueous ionic systems, *J. Chem. Phys.* 142 (2015) 184905.