

Electrodialytic removal of H₂SO₄ from its aqueous mixture with Na₂SO₄

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Abstract

The experimental results of the separation of sulfuric acid from sodium sulfate by the membrane electrolysis method have been presented. The anion-exchange membrane Neosepta ACM has been used. It has been found that the current efficiency of H₂SO₄ removal is similar for pure acid solution and for the mixture H₂SO₄-Na₂SO₄ if the initial acid concentrations are the same. For the same current density effectiveness of H₂SO₄ removal is higher for lower initial acid concentration (63% for 0.5 M and 56% for 1 M ($j = 100 \text{ mA/cm}^2$)).

1. Introduction

Electroplating is important technique used for forming metal coating. The metal coating is applied in decorative purposes, metal protection and anticorrosive purposes and for preparation functional coats. The metal surface is prepared by physical processing, washing, degreasing, etching and multiple rinsing processes before the metal coats putting on. The main environmental issues in electroplating technology is water consumption. Apart from chemical agents water is widely used for preparing electroplating baths and in rinsing processes. Important issue is a possibility of technological solutions regeneration. Working life of solution used in etching processes where main agents are inorganic acids (hydrochloric and sulfuric acid), depends on concentration of dissolved metals and concentration of acids. Taking into account economical and environmental aspects, crucial issue is an acid recovering and its separation from metal ions. One of the main membrane technique is electrodialysis (ED) which is used in many

industrial branches [1, 2]. In ED is relatively easy to separate ionic components or to purify solution from ions. Many different types of electroplating baths are used in industry. The type of bath depends on purpose of metal coat and its expected properties. The acidic baths where one of component is Na₂SO₄ are widely used in zinc coating. In this work the results of electrodialytic separation of H₂SO₄ and Na₂SO₄ in module with ACM are presented. The current efficiency of acid removal from the cathode compartment is determined. The influence of current density and concentration of H₂SO₄ on the current efficiency is described

2. Experimental

The electrolysis of sulfuric acid and sodium sulfate mixture was performed by the batch method using the membrane cell (FuMA-Tech GmbH). The Neosepta ACM (Tokuyama Co., Japan) - a strong base anion-exchange and bipolar membrane BP1 (Tokuyama Co., Japan) - were used. A scheme of the system is shown in Fig. 1. The cell was divided into 3 compartments by the bipolar and anion exchange membranes. The active area of membrane was 49 cm². The anolyte solution was a pure H₂SO₄ of low concentration (at the beginning of experiment), in the middle compartment there was a concentrated mixture of H₂SO₄ and Na₂SO₄, separated from a dilute solution of H₂SO₄ by the anion-exchange membrane ACM. The middle compartment was

separated from the cathode by the bipolar membrane. The catholyte solution was 0.5 M H₂SO₄. All the solutions were circulating through the cell compartments. After applying electric current anions moved through ACM to the anode compartment. The electric charge of anions was neutralized by protons created in the anode reaction. Because of non ideal selectivity of ACM the migration of protons in the opposite direction also took place, thus diminishing the efficiency of H₂SO₄ removal from the middle solution (Fig.1). The parameters of experiments are gathered in Tab.1. The concentration of acids was determined by the pH-metric titration (Radiometer) of samples (0.3 to 1 ml) taken during the process. The concentration of Na⁺ ions was determined by the ASA. The samples (1 ml) were taken from each compartment during the process. The mass of solutions was determined before and after the experiment.

Table 1.

The parameters of experiments: j - current density, $c_{S/2,ca}$, $c_{S/2,an,0}$ - the initial concentration of $\frac{1}{2}H_2SO_4$ in the cathode, anode compartment, respectively; $c_{Na,ca,0}$ - the initial concentration of $\frac{1}{2}Na_2SO_4$ in the cathode compartment; the volumes of solutions: $V_{ca,0} = V_{an,0} = 0.3 \text{ dm}^3$; $c_{S/2}$ refers to $\frac{1}{2}H_2SO_4$

Exper.	j [mA/cm ²]	$c_{S/2,ca,0}$ [M]	$c_{Na,ca,0}$ [M]	$c_{S/2,an,0}$ [M]
E1	100	2	1	0.1
E2	100	1	1	0.1
E3	50	2	1	0.1
E4	50	1	1	0.1
D1	0	2	1	0
D2	0	1	1	0

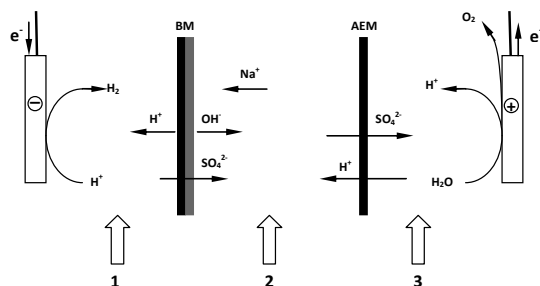


Fig. 8. The system: 1 - H₂SO₄ solution; 2 - mixture of H₂SO₄ and Na₂SO₄, 3 - H₂SO₄ solution, AEM - anion-exchange, BM - bipolar membrane

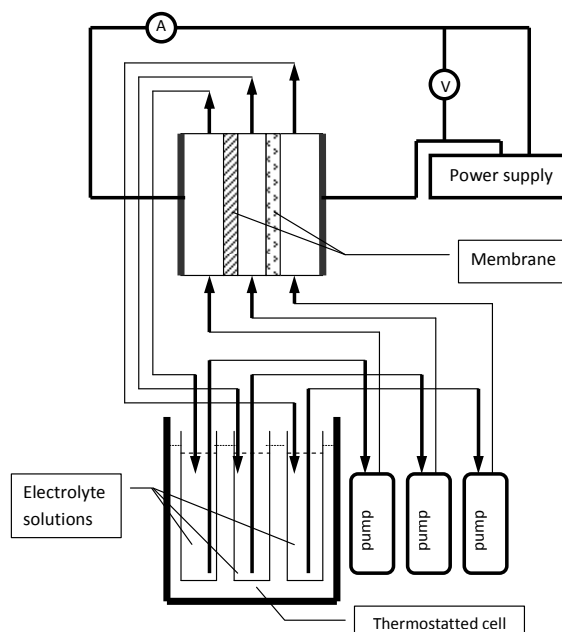


Fig. 2. The experimental setup, A - ammeter, V - voltmeter

3. Results and discussion

The concentration changes observed for the middle compartment are shown in Fig. 2. The middle compartment is on the cathode side of ACM and is denoted by the subscript "ca" ($c_{S/2,ca}$). It is seen (Fig.3) that for the experiments E1-E4 $c_{S/2,ca}$ decreases linearly with $n_F/n_{S/2,ca,0}$ in the whole range of the process. There is no significant difference between the concentration changes of sulfuric acid during electro dialysis of pure acid or of its mixture with sodium salt. The same concentration ratio $c_{S/2,ca}/c_{S/2,ca,0}$ is reached for $n_F/n_{S/2,ca,0} = 0.8$ in the case of pure acid and in the mixtures with Na₂SO₄. For $c_{S/2,ca,0} = 1 \text{ M}$ and 2 M $c_{S/2,ca}/c_{S/2,ca,0}$ is equal 0.47, 0.57, respectively. The concentration changes of H₂SO₄ for lower initial concentration ($c_{S/2,ca,0} = 1 \text{ M}$) are higher than for the more concentrated initial solution in both cases - for pure sulfuric acid and for the mixture.

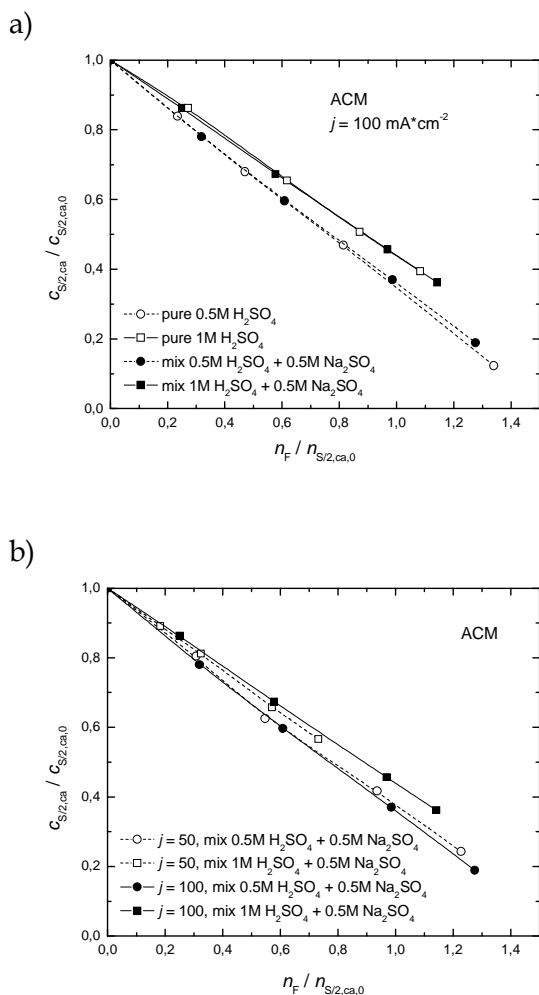


Fig. 3(a,b) Concentration of H₂SO₄ in the cathode compartment vs. $n_F / n_{S/2,ca,0}$

Comparing results of the experiments E1-E3 and E2-E4 it is seen (Fig. 2b) that the concentration changes for the same initial acid concentration are similar for both values of current density (50 and 100 mA/cm²).

3.1. Current efficiency

The efficiency of H₂SO₄ removal shown in Fig. 4 is calculated according to Eq. (1) from the changes of concentrations in the middle solutions:

$$CE_{S/2} = -V_{ca,0} \frac{dc_{S/2,ca}}{dn_F} = -\frac{dc_{S/2,ca} / c_{S/2,ca,0}}{dn_F / n_{S/2,ca,0}} \quad (1)$$

where $V_{ca,0}$ is the initial volume of cathode solution, $n_{S/2,ca,0} = V_{ca,0} c_{S/2,ca,0}$. To calculate $CE_{S/2}$, $c_{S/2,ca} / c_{S/2,ca,0}$ has been approximated as a polynomial function of $n_F / n_{S/2,ca,0}$.

The highest value of $CE_{S/2}$ is reached in E2, E4 (>0.7) at the beginning of process. For the same current density ($j = 100 \text{ mA/cm}^2$) the higher efficiency of removal H₂SO₄ at the beginning of ED is observed for lower initial acid concentration in both cases - for pure acid and in the mixture. For the same condition of experiment (current density, initial acid concentration) a slightly higher efficiency of acid removal is observed at the beginning of process for mixture solution than for pure acid (Fig. 4a). Continuing the process, CE of the mixture is lower than CE of pure acid. The addition of Na₂SO₄ has influence for decreasing the of transport numbers of SO₄²⁻ and HSO₄⁻ anions. Comparing CE for 1 M pure H₂SO₄ with that for the mixture of 0.5 M H₂SO₄ and 0.5 M Na₂SO₄ it is seen that although in both cases the total concentration of HSO₄⁻ and SO₄²⁻ anions is the same, the higher efficiency of acid removal is observed for the mixture. It is caused by the replacement of highly mobile protons by slow Na⁺ cations.

For the same concentration of Na₂SO₄ (0.5 M) in the mixture and the same j (E1, E2 - $j = 100 \text{ mA/cm}^2$ vs. E3, E4 - $j = 50 \text{ mA/cm}^2$) the efficiency of H₂SO₄ removal is higher for the lower initial acid concentration (Fig. 4b). Higher H₂SO₄ concentration causes an increased sorption of acid into the membrane and, in consequence, the decrease of membrane selectivity. The current efficiency of H₂SO₄ removal is more stable during the experiments of higher initial acid concentration (E1, E3, Fig. 4b).

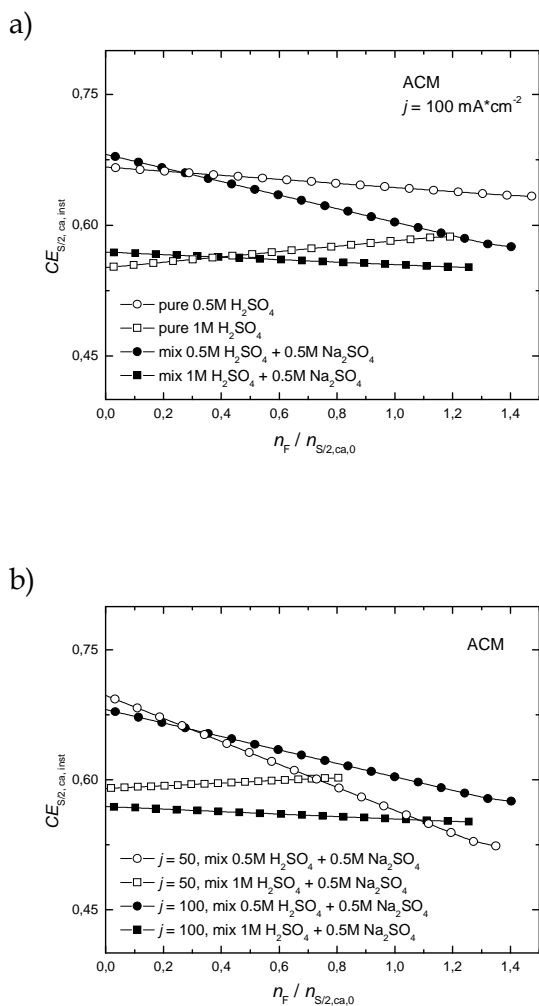


Fig.4(a,b) Instantaneous current efficiency $CE_{S/2}$ calculated from the changes of concentration of cathode solution (Eq.1), ($c_{S/2,ca}$ is approximated by a polynomial)

3.2. Diffusion

Diffusion of H_2SO_4 through the ACM membrane in both cases - using pure acid solution and the $H_2SO_4 + Na_2SO_4$ mixture - proceeds similarly (Fig.5b). Membrane permeability to H_2SO_4 for pure acid solution and for the mixture is 2.7×10^{-7} and 2.2×10^{-7} m/s, respectively (Fig.5b). In the mixture of the same initial concentration of Na_2SO_4 (0.5 M) the permeability of H_2SO_4 for 1 M (2.2×10^{-7} m/s) is lower than for 0.5 M H_2SO_4 (2.8×10^{-7} m/s). The concentration changes are shown in Fig. 5a. The diffusion of Na^+

through the ACM with the same initial concentration of Na_2SO_4 (0.5 M) but different initial concentrations of acid is similar in both cases.

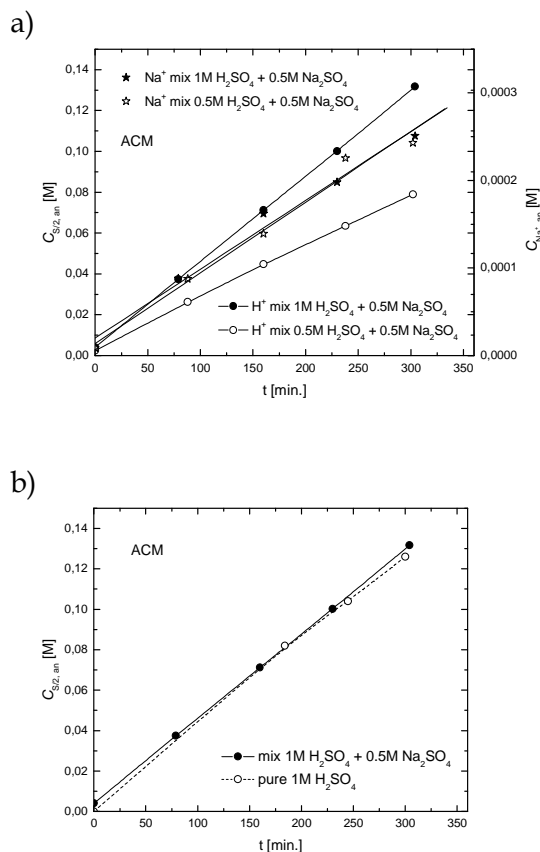


Fig.5(a,b) Diffusion of H_2SO_4 through ACM membrane

4. Conclusions

The average efficiency of H_2SO_4 removal in cathode compartment is above 56% for $c_{S/2,ca,0} = 1$ M and above 63% for $c_{S/2,ca,0} = 0.5$ M. The concentration changes of H_2SO_4 in the cathode compartment for the same initial acid concentration are similar for pure acid and for the mixture. For the same initial acid concentration in the mixture the similar concentration changes are observed in cathode compartment, independently on the current density ($j = 50$ and 100 mA/cm²). In the processes conducted at the same current

density a higher effectiveness of H₂SO₄ removal is observed for a lower initial acid concentration. The presence of Na₂SO₄ decreases the efficiency of acid removal ($\Delta CE = \text{ca. } 5\%$). However, it has insignificant effect on the diffusion of H₂SO₄.

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