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Comparison of the applicability of selected anion-exchange membranes for production of sulfuric acid by electro-electrodialysis

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ABSTRACT

Five commercially available anion exchange membranes (AEMs) were evaluated in terms of their application to concentration of sulfuric acid by electro-electrodialysis. The membrane susceptibility to acid back diffusion decreased in the following order: ACM > FAB > AAV > AMI > AM-PP. The acid current efficiency decreased with acid concentration due to the proton leakage. The highest current efficiency in wide sulphuric acid concentration range were achieved with AAV and ACM membranes. The ability to concentrate sulphuric acid with tested AEMs raised as follows: AAV >ACM > AMI > AM-PP > FAB. The highest possible concentration of sulfuric acid achieved exceeded 3.5 mol dm^{-3}, however, the usable concentration range was found to be below 1.5 mol dm^{-3}.

Keywords: Acid concentration; Sulfuric acid; Electro-electrodialysis

1. Introduction

Environmental legislations and restrictions enforce both, reduction in waste generation and increase in recovery of valuable products from wastes. Waste saline solutions, commonly generated in many technological processes, can be treated to recover acid or base to their further reuse and thus, to increase process efficiency. Electro-electrodialysis (EED) is one among two electromembrane processes, which are able to split waste salt solutions to the corresponding acid and base [1] and the only membrane method suitable for production of concentrated solutions of strong acids [1,2]. In EED, in a three-compartment stack, a salt solution is introduced to the middle compartment. Cations, transported through the cation-exchange membrane (CEM) towards the cathode, combine with OH^- ions generated by water electrolysis at the cathode, to form a hydroxide. Similarly, anions transported through anion-exchange membrane (AEM) migrate towards the anode to form acid in the anolyte. Production of acid, however, is limited by inefficiency of AEM: the back migration of protons to the diluate (to the middle compartment) results in their subsequent migration through CEM, water formation in the catholyte and a decrease in hydroxide yield [3–6]. Maximum concentration of acid to possible be achieved and its yield is thus limited by two factors: acid back diffusion and insufficient AEMs permselectivity towards protons. The latter is referred to as a *proton leakage*, as transport mechanism of protons in AEMs differs from other cations due to the proton high mobility [7,8]. The loss rate in acid yield increases with an acid concentration. What worse, the proton leakage is greater in case of polyprotic acids, such as sulfuric acid, than for monoprotic acids [7]. Nowadays, AEMs with reduced proton leakage ("*low proton leakage*"), designed for the recovery of acids, are commercially available. These exhibit satisfactory properties in diluted acids, yet in the case of concentrated polyprotic acid solutions, protons exclusion is still insufficient [9].

To ensure the economic viability of EED as a method for waste processing, its both products should be suitable for reuse, at least in the process generating the processed waste. The more concentrated acid solution, the wider possible range of application. However, due to EED efficiency loss with increasing acid concentration, a balance between

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electrical cost and product concentration must be made. Thus, the aim of this work was to find the AEM, which would be the most suitable for production of concentrated sulfuric acid by means of EED. For this purpose, we compared five commercially available AEMs in terms of extent of sulfuric acid back diffusion and proton leakage at sulfuric acid concentrations ranging from 5 to 30 wt%.

2. Methods and apparatus

Herein, five AEMs were compared, two of heterogeneous-type and three of low proton leakage-type. Their names and selected properties are listed in Table 1. Prior to experiments, each AEM was equilibrated with 5% sulfuric acid for 48 h. Thickness of each equilibrated membrane was measured with the micrometer screw.

To reduce the number of factors affecting the effectiveness of acid concentration, experiments were conducted in the two compartment EED module with only the studied AEM membrane mounted between the electrodes. The EDR-Z flat sheet electrodialyzer (MEGA, Czech Republic) with active membrane area of 64 cm^2 was used. The process solutions were circulated with a peristaltic pump (MCP, Ismatec) at a rate sufficient to assure linear flow velocities of 6 cm s^{-1}.

To quantify phenomena, which mostly affect the rate of acid concentration, two kinds of experiments were conducted. The first one were permeation experiments, which allowed to compare AEMs in terms of acid diffusion at the most unfavorable concentration gradient, to quantify the acid back diffusion. The second one were proton leakage experiments, which enable to quantify the loss of acid current efficiency with its rising concentration under the membrane's most favorable working conditions. During the course of both experiments, the concentration of sulfuric acid in solution was based on its electrical conductivity. The conductivity was measured on-line with CC-401 conductivity meter (Elmetron, Poland) equipped with CF-210 (for permeation experiments) or CF-21 (for proton leakage experiments) electrode, and recorded at 5 s intervals with PC software. Process solutions were thermostated at 25°C. All process solutions were prepared from analytical-grade salts (POCH, Poland).

In permeation experiments, the upstream solution was 500 ml of sulfuric acid of known concentration (5, 10, 15, 20 wt%), whereas downstream solution was initially 65 ml of demineralised water. The conductivity of the downstream was recorded and the current volume of solution was also measured with high accuracy (± 0.08%) by using burette with a ± 0.05 cm^3 accuracy as a flow tank.

In proton leakage experiments, the anolyte was initially 100 ml of 5% H_2SO_4, while the catholyte was 10 L of Na_2SO_4 solution of sulfates concentration 130 g dm^{-3} and pH of around 3. In this configuration, anions were transported through AEM from the catholyte (acidified Na_2SO_4) to the anolyte and formed sulfuric acid with protons generated by water electrolysis at the anode. The large volume of catholyte ensured its almost constant composition, as in a single pass mode, whereas anolyte was recirculated and its concentration increased over time. The catholyte pH was kept it the acidic range from the beginning of the experiments to prevent OH^- transport through AEM, what would lead to additional decrease in H_2SO_4 formation yield. Experiments were performed at a constant electric current density of 750 A m^{-2} for 10 h, which corresponded to total electric charge of 48 Ah. The volume of the anolyte was measured at the beginning and at the end of each experiment and its linear change over time was assumed.

3. Results and discussion

3.1. Acid back diffusion

Diffusion is inevitable in electromembrane processes and may lead to product or efficiency loss. Back diffusion results from concentration gradient across the IEM and increases with an increase in the concentration ratio between the streams separated by IEM.

Basing on the concentration of acid in the downstream solution and its volume, we calculated the molar steady-state flux of acid through the AEM according to Eq. (1):

$$\mathrm{J}= \frac{1}{\mathrm{s}}\frac{dn}{dt} \tag{1}$$

where is the *J*- molar steady-state flux of acid, mol (m^{2}s)$^{-1}$; *n* is the number of moles of sulfuric acid transported to downstream solution, mol; *t*- time, *s*; *s* is the geometric area of membrane, m^2.

As the linear velocity of solution was high (6 cm s^{-1}), it was assumed that the turbulent flow inside the chamber made the impact of concentration polarization in the EED

Table 1
Characteristics of anion exchange membranes used in the study (measured thickness and other properties as specified by the manufacturer)

Membrane	Type	Character	Functional groups	Ion exchange capacity, meq/g	Thickness, mm
AAV, Selemion	Low proton leakage	Weak base	n/a 4-vinylpyridinium,according to [10]	0.95^a	0.11
ACM, Neosepta	Low proton leakage	Strong base	Quaternary ammonium	1.4-1.7	0.1
AM-PP, Ralex	Heterogeneous	Strong base	Quaternary ammonium	1.8	0.56
AMI-7001S, Ultrex	Heterogeneous	Strong base	Quaternary ammonium	1.3 (1.01^a)	0.45
FAB, Fumasep	Low proton leakage	n/a	n/a	>1.3	0.14

^{a}, by dry mass; n/a, no data available.

chamber adjacent to the AEM negligible. Thus, concentrations in the bulk solution and at the membrane surface were assumed to be equal. Fig. 1 illustrates the relation between the calculated acid flux and concentration of sulfuric acid in the upstream solution.

In Fig. 1, it can be clearly seen that at the studied concentration range, in each case sulfuric acid flux through AEM increased linearly with the increase of acid concentration in upstream solution. It confirmed negligible role of concentration polarization on acid concentration in the downstream solution. The change in acid flux through AEM with acid concentration allowed to calculate the apparent mass transfer coefficient (describing the transport through the membrane and its adjacent polarization layers) of sulfuric acid through each AEM according to Eq. (2):

$$k_{app} = \frac{dJ}{dc} \tag{2}$$

k_{app} is the apparent mass transfer coefficient, m s^{-1}; c- upstream acid concentration, mol m^{-3}

In Table 2, the calculated values of k, together with its standard error and determination coefficient (r^2) for each membrane tested, are given.

The fluxes of sulfuric acid were the largest for ACM and FAB membranes, and the smallest for AM-PP membrane (Fig. 1). This could be linked to thickness of AEMs, as it was, in fact, the length of diffusion path. At the investigated concentration range (5–30% wt.), thick, heterogeneous membranes were found to be more effective in restraining the sulfuric acid diffusion than thin, homogeneous membranes, even besides declared reduced proton transport.

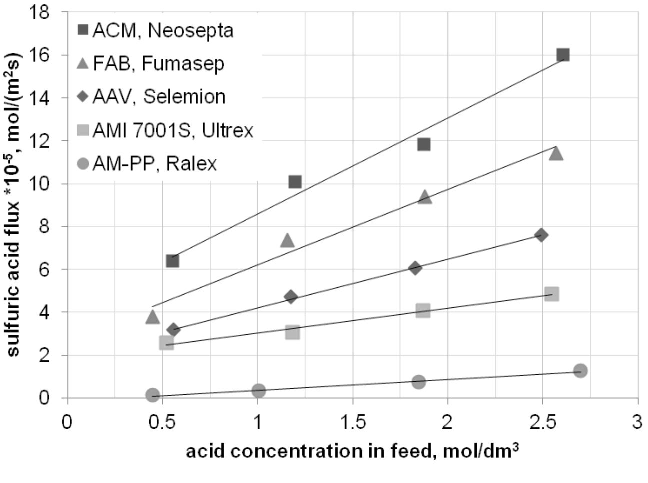

Fig. 1. Molar flux of sulfuric acid upon acid concentration in upstream solution.

Table 2
Apparent mass transport coefficients determined for tested AEM membranes

Membrane	k_{app} 10^{-8}, m s^{-1}	SE 10^{-8}	r^2
AM-PP, Ralex	0.51	0.04	0.9894
AMI 7001S, Ultrex	1.16	0.11	0.9840
AAV, Selemion	2.26	0.05	0.9990
FAB, Fumasep	3.52	0.36	0.9791
ACM, Neosepta	4.47	0.44	0.9808

3.2. Proton leakage

According to the model of membrane acidic and alkaline state proposed by Jorissen [4], when AEM separates two acidic solutions of sufficient concentration, the current efficiency of acid on the anode side depends solely on the acid concentration in anolyte. This is called an acidic state of AEM. The decrease of acid yield due to competitive transport of OH$^-$ through AEM does not occur, as neutralization occurs in the polarization layer on the cathode side of the AEM. The validity of this model is supported by the extensive literature data [1,3,6,8,10].

In our two chamber experimental setup, equal amounts of protons and hydroxide ions were generated by water decomposition on respective electrodes (100% electrodes yield was assumed). The sulfuric acid was produced by combination of protons generated at the anode with sulphates transported through the AEM, due to the electroneutrality requirement. Under the experimental conditions (large volume of acidified catholyte providing constant concentration, high concentration of sodium sulfate in the catholyte, high flow rate), the conditions for the acidic state of AEM, according to Jorissen model [4], were fulfilled. Therefore, the flux of sulfates through AEM was the highest, as it did not decrease by the competitive transport of OH$^-$ and the highest production rate of sulfuric acid was obtained. Investigation on concentration of sulfuric acid using different AEMs under such conditions allowed to reliably compare them in terms of their suitability for the preparation and concentration of sulfuric acid by means of EED.

Fig. 2 illustrates the changes in sulfuric acid concentration in the anolyte during proton leakage experiments. As shown, the final concentration of acid after 600 min, what corresponded to the electric charge of 48 Ah, varied from 3 to

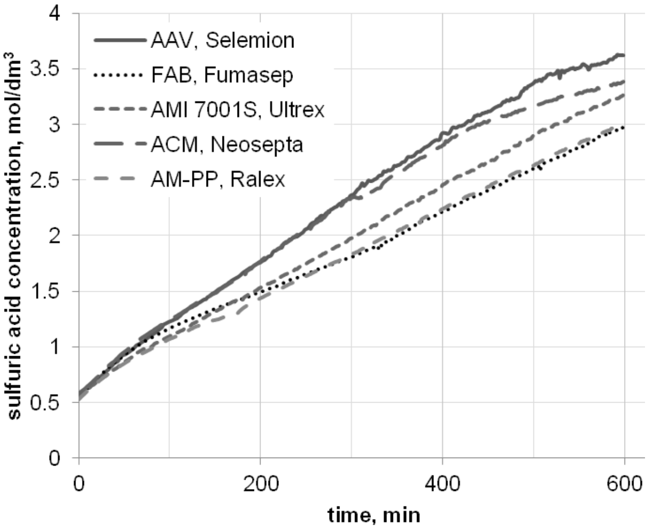

Fig. 2. The changes of sulfuric acid concentration rate during proton leakage experiments.

3.6 mol dm^{-3} and was the highest for AAV membrane and the lowest for both, FAB and AM-PP membranes. Curves for ACM and AAV membranes approached the plateau, thus the maximum H_2SO_4 concentration. Yet, apart from two low proton leakage membranes, which outstand other ones (AAV and ACM), the FAB membrane performance was similar to that of the heterogeneous membrane AM-PP. The obtained results did not consist with back diffusion results determined in the previous section and it was apparent that the main origin of acid yield loss was not back diffusion. In Fig. 2, three stages of acid concentration can be distinguished. At the very beginning, the concentration rate was similar for all membranes and started to differentiate above about 1 mol dm^{-3} acid. In the middle stage, the acid concentration rate was individual for each membrane, and, at the end, it decreased rapidly for some membranes (AAV, ACM).

Because of the volume change of anolyte in the course of process, a simple comparison of changes in concentration was unreliable, and the current efficiency (CE) needed to be used as an indicator of the electric current utilization for ion transport. In the absence of the competitive OH$^-$ transport trough AEM, the reason of CE loss could be simple back migration of protons due to insufficient AEM permselecivity. Thus, the proton leakage could be expressed as 100-CE. The (cumulative) current efficiency was calculated according to Eq. (3):

$$CE = \frac{100\% \cdot \Delta m}{m_h \cdot I \cdot t} = \frac{\left| V_t \cdot C_t - V_0 \cdot C_0 \right|}{m_h \cdot I \cdot t}, \% \tag{3}$$

where, *CE* is the current efficiency, *I* is the current, A; *t* is the time, s; *V* is the volume, dm^3; *C* is the concentration, g dm^{-3}, m_h is the electrochemical equivalent, g (A·s)$^{-1}$

As shown in Fig. 3, *CE* of acid formation decreased in the course of experiment, in case of all membranes. This was probably caused by an increase in acid concentration in the anolyte and its related increase in sulfuric acid back-diffusion rate.

CE-values obtained in this work do not reflect *CE*s envisioned in a real EED process, in which other factors, such as salt concentration in the diluate, may strongly affect process. However, they allowed comparing the tested AEMs in terms of their applicability for EED. As shown in Fig. 3, initially high *CE* decreased rapidly with the increase of acid concentration in anolyte until the value in the range of 1.25–1.5 mol dm^{-3} was obtained. After that, CE remained approximately constant with H_2SO_4 anolyte concentration up to approximately 3 mol dm^{-3}, when it again started to rapidly decrease. The highest initial *CE* of acid was observed for FAB membrane, for which, however, the highest rate of *CE* decrease with anolyte H_2SO_4 concentration increase was observed. The lowest initial *CE* was observed for AM-PP membrane; the heterogeneous AMI membrane revealed similar results. The highest average *CE*s in a wide acid concentration range were observed for AAV and ACM membranes.

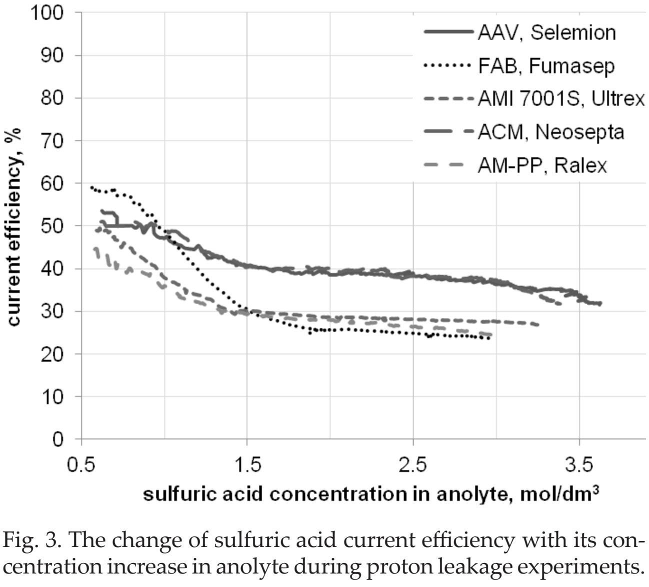

Fig. 3. The change of sulfuric acid current efficiency with its concentration increase in anolyte during proton leakage experiments.

The comparison of AEMs behaviour during non-current and current process allowed concluding that the back diffusion played an important role in sulphuric acid concentration by EED. However, the acid efficiency was lost mostly due to the proton leakage. Heterogeneous membranes used in the study, despite their low acid diffusion rates, showed higher proton leakage rates, thus low acid production efficiency. These results are consistent with the literature [6], where some other commercial AEMs (Electropure Excellion I-200, Sybron Ionac MA-3475 and MA-7500, GE Ionics AR204-SZRA) were compared in terms of their applicability to electromembrane conversion of sodium sulfate into sodium hydroxide and sulfuric acid. Among all tested AEMs Sybron Ionac MA-7500 revealed the highest permselectivity, however, the acid concentration was maintained below 1 mol dm^{-3}.

4. Conclusions

The aim of this work was to compare five commercially available AEMs (Selemion AAV, Neosepta ACM, Ralex AM-PP, Ultrex AMI-7001S, Fumasep FAB) in terms of back diffusion and proton leakage rates, to find the most suitable AEM for production of concentrated sulfuric acid by means of EED. It was found, that sulfuric acid formation current efficiency decreased with the anolyte acid concentration increase, and the rate of efficiency loss varied between membranes. The sulphuric acid efficiency loss was rather caused by insufficient permselectivity of membranes than by the acid back diffusion. Low proton leakage membranes were more effective in concentration of acid than thick, heterogeneous membranes. Among heterogeneous AEMs, Ultrex AMI-7001S surpassed Ralex AM-PP. The highest current efficiency was achieved with Fumasep FAB for the dilute acid, while for concentrated acid with Selemion AAV. It should be also emphasized, that while the highest possible concentration of sulfuric acid, which can be achieved in EED, exceeds 3.5 mol dm^{-3}, the drop of current efficiency practically limits usable concentration of H_2SO_4 to under 1–1.5 mol dm^{-3}.

These conclusions are important for the selection of an appropriate membrane to particular ED processes such as electro-electrodialysis or bipolar membrane electrodialysis in conversion of waste salt, which are used to acid production. Higher acid recovery and an increase in electrical energy utilisation undoubtedly would have positive environmental impact. On the other hand, these are also key factors in terms of commercial viability of process.

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Symbols

c	—	Upstream acid concentration, mol m^{-3}
C	—	Concentration, g dm^{-3}
CE	—	Current efficiency, %
I	—	Current, A
J	—	Molar steady-state flux of acid, mol (m^{2}s)$^{-1}$
k_{app}	—	Apparent mass transfer coefficient, m s^{-1}
m_{h}	—	Electrochemical equivalent, g (A s)$^{-1}$
n	—	Number of moles of sulfuric acid transported to downstream solution, mol
s	—	Geometric area of membrane, m^2
t	—	Time, s
V	—	Volume, dm^3

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