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The development of electrodialysis modules for specific applications

Lukáš Václavík[a], Natália Káňavová[b,*], Lubomír Machuča[b], Marek Doležel[b], Michal Amrich[b], David Tvrzník[b]

[a]*MEGA a.s., Pod Vinicí 87, 471 27 Stráž pod Ralskem, Czech Republic, Tel. +420 606 671 828; email: lukas.vaclavik@mega.cz*
[b]*MemBrain s.r.o., Pod Vinicí 87, 471 27 Stráž pod Ralskem, Czech Republic, Tel. +420 725 862 562; email: natalia.kanavova@membrain.cz (N. Káňavová), Tel. +420 602 506 423; email: lubomir.machuca@membrain.cz (L. Machuča), Tel. +420 727 942 655; email: marek.dolezel@membrain.cz (M. Doležel), Tel. +420 601 384 729; email: michal.amrich@membrain.cz (M. Amrich), Tel. +420 607 518 428; email: david.tvrznik@membrain.cz (D. Tvrzník)*

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ABSTRACT

In presence, there is a crucial demand to produce electrodialysis (ED) modules customized for specific applications in order to take full advantage of membrane modifications and different module constructions and arrangements. Goal of this work was to examine and describe ways to develop ED modules and their components with the emphasis on the special use they are intended for. The possibilities of how to do this are e.g. the use of low-cost alternatives of ion-exchange membranes and other materials, unusual structuring of membrane stack or hydraulic streams, the use of tortuous spacers to achieve deep desalination in single-pass flow regime, or stack modification in order to get high concentration in concentrate stream. These modifications could help to optimize efficiency and costs of the ED technology and performance, and to extend the application field of the process of ED.

Keywords: Desalination; Electrodialysis; Low-cost materials; ED module design

1. Introduction

1.1. Electrodialysis principle

Electrodialysis (ED) is an electrically driven membrane separation process able to separate electrolytes from solutions. The device intended for ED is called ED module and it is composed of tightening boards with electrodes on their inner side, and a membrane stack placed between them. The membrane stack consists of alternatively arranged cation-exchange membranes (CEM) and anion-exchange membranes (AEM) separated by spacers providing the space for liquid flow and its appropriate mixing. Conventionally, three hydraulic circuits take place in the ED module—diluate, concentrate, and electrode solution circuit. The compartments defined by CEM facing to the cathode side and AEM to the anode side of the stack are for the diluate flow, and the compartments defined by CEM on the anode side and AEM on the cathode side are for the concentrate flow. The arrangement of membranes in the stack ensures that cations and anions are

*Corresponding author.

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almost selectively transported through CEMs and AEMs, respectively. Thus, ions are displaced from diluate circuit, where the solution is diluted, to concentrate circuit, where the solution is concentrated. The role of electrode solution is to flush electrodes and remove gases generated by electrode reactions. The spacer is usually formed by a frame and turbulization net or system of counters forcing the liquid to change the flow direction. By this manner, the liquid is transversely mixed and the mass transfer is enhanced.

Nowadays, there is a significant effort to design "customized" ED modules and technological units. Devices should be adapted and modified according specific requirements of each application to be able to perform their properties and abilities in the best and most effective way. There is a great scope for the development or modification of ED modules.

1.2. Stack structure

The typical stack structure is depicted in Fig. 1 and enables only conventional ED desalination of one stream (diluate) and concentration of the another stream (concentrate). By changing the membrane stack structure or the number of hydraulic circuits, a wide range of new application possibilities appear. If the stack is composed of only one type of ion-exchange membrane (CEM or AEM), the ED module serves as continuous ion exchanger. As shown in Fig. 2, it can be used e.g. in water softening [1] or for recovery of lactic acid from sodium lactate [2]. In another type of module, the pair of CEM/AEM and one membrane of another kind is the repeating structure. In such case, there are three main hydraulic circuits—diluate, concentrate, and product stream. In product stream, only the ion exchange takes place. This can be used e.g. in fruit juice deacidification [3] (Fig. 3). If the typical stack structure is kept, but the number of hydraulic circuits is changed from two to four, the module can be used for metathesis (Fig. 4). This was applied e.g. in ionic liquids production [4] or for lactic acid recovery from fermentation broth [5].

1.3. Tortuous spacer

In ED, the desalination cut in single-pass flow regime depends on the flow channel length. Long flow channel, and thus high desalination cut, could be achieved either in multistage module arrangement or in only one module by using tortuous spacers. The limitation of these conceptual solutions is only the pressure drop in the series of stacks or in single stack. The negatives of multistage arrangement are constructional difficulty and lower reliability of the system caused by inlet pressure differences of diluate and concentrate at the stages, and internal leakages of diluate and concentrate. These are reasons for the development of ED stack with tortuous spacers, where the sufficient channel length is achieved in one stage.

Regarding the design of ED spacer, the main requirements for a good performance are a small interelectrode distance, adequate means for maintaining the dimensions of the cell, a uniform fluid distribution, and the promotion of a good rate of mass transport. In the tortuous flow path spacer, flow starts from one corner of the membrane and follows a serpentine path, defined by the shape of the spacer, to the opposite corner of the membrane [6,7].

In order to develop the design of tortuous path spacer, the method of limiting cut prediction [8] can be used, which enables to calculate the flow channel length and width according to required desalination cut and production capacity.

1.4. Concentration of electrolyte solutions

The increase in concentration of solutions without the necessity of phase change can be interesting for many producers not only in chemical industry. In the

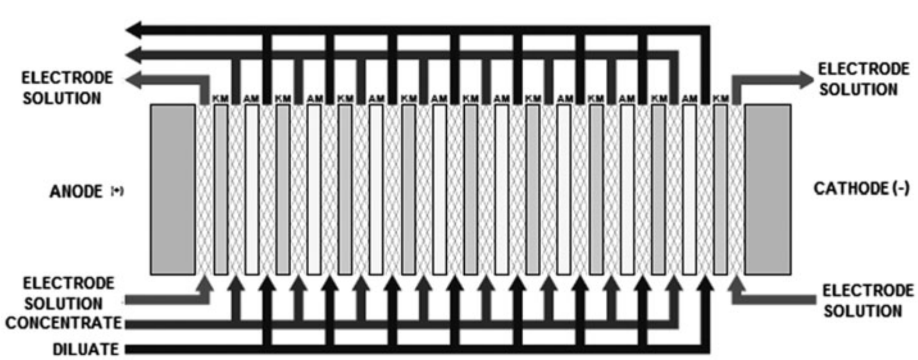

Fig. 1. Typical ED stack structure.

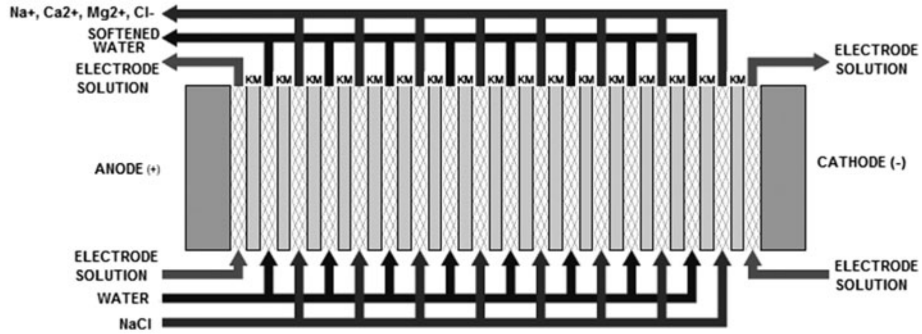

Fig. 2. ED stack composed of CEMs for water softening.

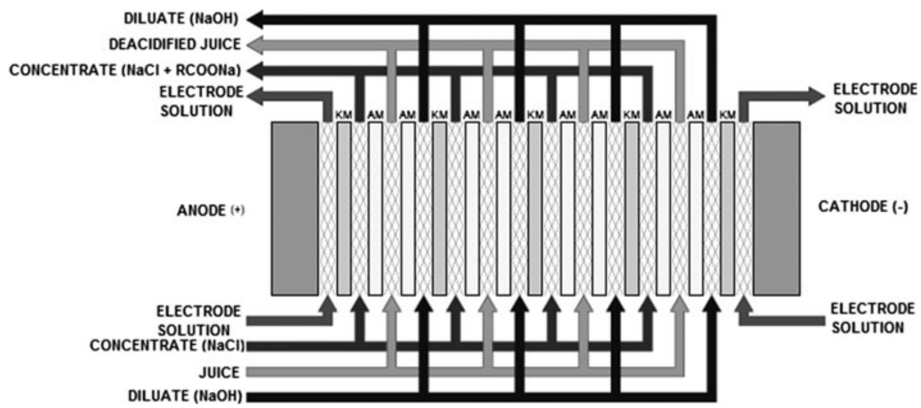

Fig. 3. Three-circuit ED stack for juice deacidification.

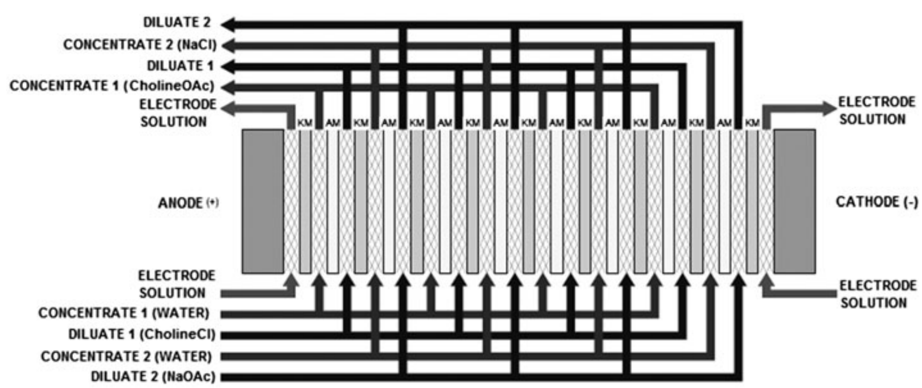

Fig. 4. Ionic liquid production by means of metathesis (four-circuit ED stack).

case of vacuum evaporator, which is a traditional way of concentration, the operational costs depend on the amount of evaporated water. On the other hand, the operational costs of ED process are dependent on the amount of electrolyte transported through membranes. The amount of solution entering the vacuum evaporator could be significantly decreased by ED pretreatment which leads to considerable energy savings. Moreover, the diluate stream can be returned to the technology and used as process water. There are some risks about the production of solutions with very high concentration. Among these, the "leakage current" and back diffusion can be mentioned as the most relevant. Leakage currents are the consequence of conductive connection of the compartments in ED module made by distribution channels of diluate and concentrate. The higher the conductivity of streams, number of membrane pairs, or applied voltage, the higher the leakage currents. As a result of leakage current, the current efficiency is decreased and energy demands are increased and a great risk of stack damage appears. In terms of electrolyte back diffusion from concentrate to diluate, its driving force is high concentration difference between the solutions. Consequently, the separation rate and current efficiency are decreased.

Possible solution can be the use of non-flow-through concentrate spacers in which the concentrate is formed only by transported salts and water from diluate stream through membrane and it is removed by a system of discharge channels in spacer frames. Similar principle was applied also by Zabolotskii et al. in lithium chloride concentration [9]. If the sufficient current density is applied, the concentration in concentrate can be up to 200 $g\,l^{-1}$.

1.5. Low-cost ion-exchange membranes

Membrane foils were developed in order to reduce production costs and to decrease membrane resistance. Membrane foils are made of only ion-exchange resin and inert polymer matrix without the use of reinforcing fabric. The negative quality of foils is their increased flexibility and decreased mechanical strength. Due to this fact, it is not possible to achieve satisfactory internal tightness with spacers that are conventionally used with membranes reinforced with fabric and it is necessary to develop new kind of spacer able to provide foils sufficient support.

2. Experimental

In experiments, laboratory and pilot ED modules were provided by MemBrain, Stráž pod Ralskem, Czech Republic. Ion-exchange membranes Ralex® and membrane foils were provided by MEGA, Stráž pod Ralskem, Czech Republic.

2.1. Lactic acid production by three-circuit ED module

The production of lactic acid from sodium lactate was examined using the three-circuit ED stack structure (CEM-CEM-AEM). In this structure, the sodium ion was substituted by H^+ ion from nitric acid. Laboratory ED module with 10 membrane triplets (64 cm^2 of active membrane area) was used in experiments working in feed and bleed mode. The current density was kept constant at the value of 25 $mA\,cm^{-2}$ and circulating flow velocity was 6 $cm\,s^{-1}$ in each circuit. The initial sodium lactate concentration in product stream was 20 wt.% and nitric acid concentration in diluate stream was 3 wt.%. In concentrate circuit, there was the solution of sodium nitrate with the initial concentration of 2 wt.%. After the series of tests with the duration of 4.5 h, ED performance parameters were evaluated. Experiments were made repeatedly to ensure high reliability of results.

2.2. Deep desalination by ED module with tortuous spacers

In Fig. 5, there are some proposals of tortuous spacer design for pilot ED module. Length and width of their channels were calculated in accordance with the requirement of 80% single-pass desalination of diluted solutions (up to 5 $g\,l^{-1}$). The flow of liquid in proposed spacers was visualized in transparent testing cell to find out if there are some leakages through channel separators and to assess the flow distribution. The best option in terms of flow distribution and internal tightness stability was variant A (Fig. 5). The pilot ED module with 25 membrane pairs of 1 m^2 active membrane area and such spacers (Fig. 5) was tested for the desalination of sodium chloride solution in single-pass flow regime and desalination cuts were evaluated for different process conditions. The concentration of sodium chloride was in the range of 1–5 g l^{-1}, applied voltage was up to 50 V and linear flow velocity was 4.4 or 5.9 $cm\,s^{-1}$.

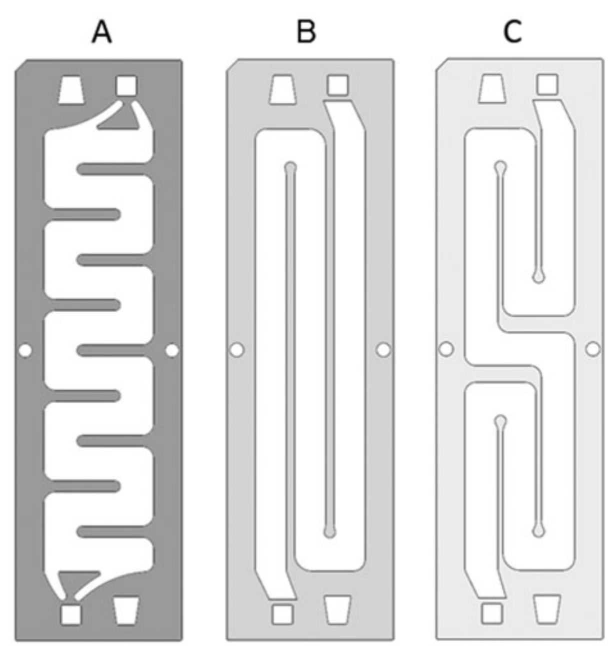

Fig. 5. Proposals of tortuous spacer design.

2.3. ED concentration of sodium sulfate

The laboratory ED module with 10 membrane pairs (64 cm^2 of active membrane area) was used for the concentration of sodium sulfate solution. Special non-flow-through spacers with discharge channels in the frame designed for this purpose were used as concentrate spacers. The initial concentration of sodium sulfate in diluate circuit was 20 $g\,l^{-1}$. Circulation flow velocity of diluate was 5 $cm\,s^{-1}$ and applied voltage was 10 V. Concentrate was collected in a container placed below the module. Experiments were carried out until the concentration in diluate circuit was below 0.5 $g\,l^{-1}$. Measurements were made in triplicates.

2.4. Membrane foils testing

The conventional spacer was adapted especially for flexible membrane foils by replacing traditional distribution channels by strong plastic net. After that, the desalination experiments were carried out and benefits of using membrane foils were evaluated. The electrical resistance of membrane foils used in experiments was approx. one half of the resistance of standard ion-exchange membranes Ralex® with reinforcing fabric (resistance of standard membranes is 6.9 Ω cm^2). The pilot ED module with 25 membrane foil pairs (1 m^2 of active membrane area) was equipped with membrane foils and modified spacers. The solution of sodium sulfate with the concentration of 20 $g\,l^{-1}$ was desalinated in batch regime with the applied voltage of 25 V using circulation flow velocity of 4.2 $cm\,s^{-1}$. Experiments were stopped after the concentration in diluate decreased below 0.5 $g\,l^{-1}$. Measurements were repeated four times.

3. Results

3.1. Lactic acid production

In Fig. 6, concentration profiles of lactic acid and sodium ions in product stream are shown in time. Sodium ion is a product pollutant in this case, as it is replaced by H^+ ion forming lactic acid. In the time of approx. 180 min, the concentration of lactic acid reached its maximum and the one of sodium decreased close to zero. In Table 1, evaluated characteristics of ED process are summarized. Produced lactic acid was of high purity and very high concentration. Also current efficiency was relatively high. It indicates that used membrane stack arrangement was chosen reasonably for this purpose and it is promising for future scale-up process.

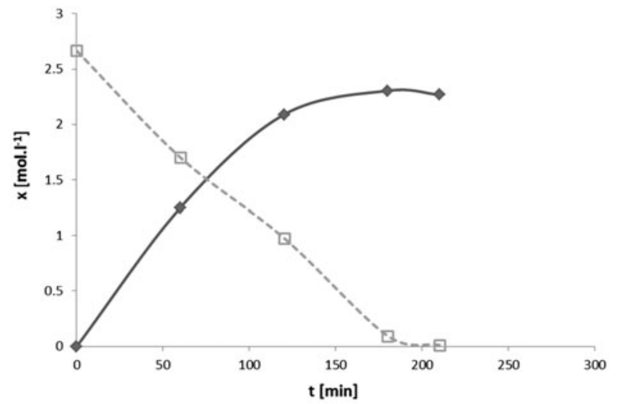

Fig. 6. Concentration profiles of lactic acid (full line) and sodium ions (dashed line) in product stream in time.

Table 1
Characteristics of lactic acid (LA) production by three-circuit electrodialysis

Concentration of LA ($g\,l^{-1}$)	223
Purity (%)	99
Current efficiency (%)	74
Energy consumption ($W\,h\,kg^{-1}$)[a]	585

[a]Energy consumption per 1 kg of pure lactic acid.

3.2. Deep desalination

In Table 2, obtained desalination parameters at different inlet sodium chloride concentrations are listed. In this case, applied voltage was 25 V and linear flow velocity was 4.4 $cm\,s^{-1}$. In Figs. 7 and 8, there are dependences of determined desalination cuts on inlet

Table 2
Desalination characteristics of ED module with tortuous spacers at 25 V and flow velocity of 4.4 $cm\,s^{-1}$

Concentration of NaCl ($g\,l^{-1}$)	1	2	3	4	5
Desalination cut (%)	80.6	76.5	70.1	64.4	56.2
Energy consumption ($W\,h\,l^{-1}$)[a]	0.381	0.742	1.021	1.266	1.453
Current efficiency (%)	98.1	97.5	97.2	93.7	89.6

[a]Energy consumption per 1 l of product water (diluate).

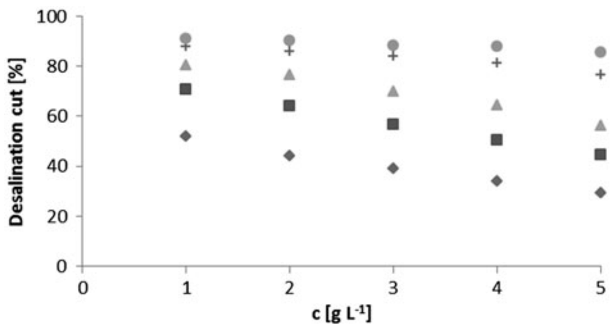

Fig. 7. Dependence of desalination cut on inlet NaCl concentration at linear flow velocity of 4.4 cm s^{-1} and voltages of ♦ 12.5 V, ■ 18.75 V, ▲ 25 V, + 37.5 V, and ● 50 V.

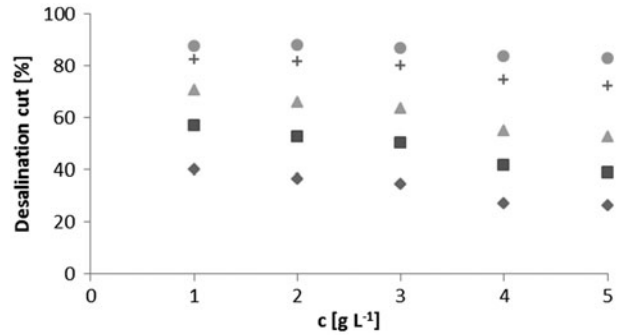

Fig. 8. Dependence of desalination cut on inlet NaCl concentration at linear flow velocity of 5.9 cm s^{-1} and voltages of ♦ 12.5 V, ■ 18.75 V, ▲ 25 V, + 37.5 V, and ● 50 V.

Table 3
Process parameters of sodium sulfate concentration by electrodialysis

Type of concentrate spacers	Concentration of Na_2SO_4 (g l^{-1})	Current efficiency (%)	Energy consumption (W h kg^{-1})[a]
Conventional	39.5	91.4	633
Non-flow-through	174.4	90.3	590

[a]Energy consumption per 1 kg of transported salts.

Table 4
Results of batch sodium sulfate desalination experiments

Membrane type in ED module	Desalination time (min)	Current efficiency (%)	Energy consumption (W h kg^{-1})[a]
Standard	105	83	456
Membrane foils	70	92	388

[a]Energy consumption per 1 kg of transported salts.

sodium chloride concentration at different applied voltages and flow velocities. It is clear that desalination cut decreased significantly with increasing inlet electrolyte concentration. As shown in Table 1, desalination cut decrease was almost 25% abs. comparing inlet concentrations 1 and 5 g l^{-1}. But Figs. 7 and 8 imply that the higher applied voltage, the less pronounced the decrease. Naturally, energy consumption per 1 l of product (desalinated water) was the highest when the solution with the highest inlet concentration was processed, as the highest amount of salt had to be removed to concentrate. Consequently, ED module with appropriate design of tortuous spacer is able to desalt deeply dilute solutions of electrolytes. Desalination cut can be controlled either by linear flow velocity of processed solutions or by applied voltage according to requirements.

3.3. Concentration of sodium sulfate

The results of concentration experiments made on ED module with non-flow-through concentrate spacers are presented in Table 3 in comparison with the results obtained on module with conventional spacers. Undoubtedly, non-flow-through spacer enabled to obtain much higher concentrations of electrolyte than the conventional one. Current efficiency was comparable in both the cases, so that the effect of "leakage currents" was insignificant. Energy consumption per 1 kg of transported salts was even lower in the case of the module with non-flow-through spacers. Obtained results show that conceptual design of non-flow-through spacer is suitable for the use in the field of electrolyte concentration and for the elimination of undesirable effects coupled with such process.

3.4. ED module with membrane foils

In Table 4, the results of batch desalination tests using ED module with membrane foils are showed and compared to results obtained with the module equipped with standard membranes. All examined parameters were more favorable in the case of module with membrane foils. Desalination time was 30% shorter, energy consumption 15% lower, and current efficiency 9% abs. higher in comparison with standard module. These data indicate that the use of low-cost alternative of standard ion-exchange membranes with lower electric resistance could be very beneficial, mainly in the case of more concentrated solutions processing when the membrane resistance is the highest resistance in membrane stack, so that it determines ED performance.

4. Conclusions

- Possibility of the use of three-circuit ED module for lactic acid production from sodium lactate was confirmed. Moreover, obtained lactic acid concentration, purity, and other process parameters are very promising for further development and scale-up to larger technology.
- ED module with especially designed tortuous spacers was able to desalt sodium chloride solutions with the concentration 1–5 $g\,l^{-1}$ in single-pass obtaining high desalination cuts (up to 90%). Desalination cut strongly depended on inlet salt concentration.
- The module with non-flow-through concentrate spacers was able to concentrate sodium sulfate solution from 20 to 175 $g\,l^{-1}$. The comparison with conventional module showed that current efficiency was similar in both the cases, so that non-flow-through spacers really eliminated the effect of "leakage currents".
- Low-cost alternative of standard heterogeneous membranes Ralex® with lower electric resistance could be used in ED module with modified spacers and sufficient internal thickness could be attained. The use of membrane foils is very promising, as it can shorten desalination time, decrease energy consumption and increase current efficiency of the process.

Acknowledgments

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