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RESEARCH ARTICLE

Production of Lactic Acid by Ion Substitution in 3-Compartment Electrodialysis and Comparing of Stack Arrangements

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Abstract
Electrodialysis (ED) is a process which is to transport anions and cations selectively and remove them from solutions and concentrate to the other ones. In three-compartment electrodialysis it is possible to immobilize required ions in certain ED compartment and change their counterions. In laboratory electrodialysis unit sodium lactate model solution was tested for conversion onto lactic acid via ion substitution. Four different arrangement of streams and membrane arrangement were compared in membrane stack the process was described. Mole and mass flux, reached product purity and energy consumption were evaluated for all examined cases.

Keywords
ion substitution, lactic acid, electrodialysis

1 Introduction

Some organic acids, like citric acid, lactic acid, succinic acid, etc., are in general used in food industry as acidity regulators, antioxidants or preservatives [2,18]. So as, they are used as precursors of bio-degradable polymers eg. polylactide (PLA), poly(lactide-co-glycolide) (PLGA), poly(butylene succinate) (PBS), polyaspartic acid (PAA). They are used in pharmacy [10,17] or more and more frequently as packaging materials [4,12,20]. Increasingly, they are produced by environmental-friendly fermentation of glucose, starch, molasses [5,6,9,14,16,19]. The fermentation broth is neutral or weakly alkaline mixture of saccharides, organic and inorganic salts and fermentation microorganism [6,15]. First, the acid separation is done by broth ultrafiltration to remove microorganisms and some large proteins [6]. The second step is converting, purifying and concentrating the organic acid solution [7,8], commonly using strong acid or ionic liquid [21] extraction.

The aim of this work is to evaluate opportunities of non-conventional three-compartment structure of electrodialysis membrane stack on laboratory unit (P EDR-Z/4x, MemBrain s.r.o.) and find out the best arrangement for producing the organic acid from its salt by electrodialysis substitution (ED-S) process. Substitution, in this case, means the metathesis focused on purity of only one ion type. More common process of four compartment metathesis [3,8,11] is used for ionic double decomposition. The reaction rate in four compartment ED is highly limited by mobility of the slowest ion though the membrane. Using ED-S enables to make similar process with large ions with higher rate.

For example, by using ED-S is possible to produce weak acids without displacing them from their dissolved salts by strong acid followed by expensive and energy demanding distillation or crystallization. So that high acid purity due to non-mixing of unwanted ions can be reached.

Testing was carried out with sodium lactate (LacNa) solution and nitric acid (HNO_3) as proton donor. Lactate anion shows lower diffusivity and weaker ability to migrate through membrane in comparison to H^+ ion which is the most movable ion ever. Primarily lactic (LacH) acid and secondarily sodium nitrate ($NaNO_3$) were produced.

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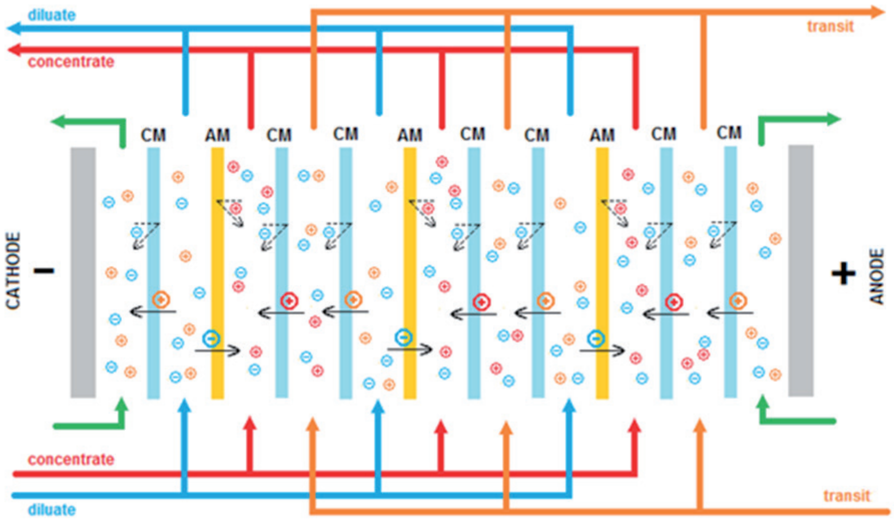

Fig. 1 Schematic ion transport in three triplet-unit ED module, CM doubled.

2 Experimental

ED module was arranged from 10 membrane triplets of 64 cm^2 membrane active area. The cation exchange membranes (CM) were doubled in the first and second cases and the anion exchange membranes were doubled in the third and fourth cases. The chamber (stream) between the same membranes was called "transit" (T), see Fig. 1. Ions of certain polarity, which could not pass through the membranes due to selectivity, were immobilized in T. The cations could pass only through the cation-selectively membranes (CM) and anions could pass only through the anion-selectively membranes (AM). So the ions immobilized in transit chambers are determined by coupled polarity of the membranes. Four sets of experiments were done for different immobilized ions – lactate and nitrate anions, sodium and hydrogen cations, see Fig. 2 a-d. Testing was performed in feed&bleed mode under current density of 25 mA.cm^{-2}. Membranes were distanced by 0.8 mm turbulence net spacer and solutions flow was 70 l.h^{-1}. Electrode rinsing solution was 20 g.l^{-1} $NaNO_3$ solution.

The initial stream composition of diluate (D), transite (T) and concentrate (C) in all four cases are shown in Table 1. They can be sorted in by the type of doubled membrane – transit chamber made of two CMs immobilizes anions (cases 1,2) and two AMs immobilizes anions (cases 3, 4) between them. The product streams were in cases 1 and 4 the transites and in cases 2 and 3 the concentrates.

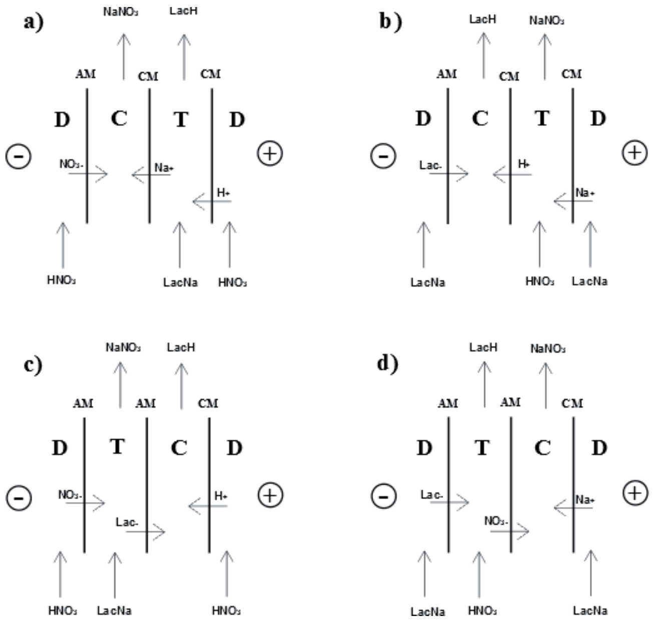

Fig. 2 Arrangements of tested cases:
a) case 1, in T immobilized lactate ions, sodium ions replaced by H^+
b) case 2, in T immobilized nitrate ions, protons meet lactate in C
c) case 3, sodium ions immobilized in T, lactate meet proton in C
d) case 4, hydrogen cation immobilized in T, lactate ion replaces nitrate ion

The testing was set up for 4.5 hours, as this duration seemed to be sufficient for process study. Specific conductivity, pH and temperature of all streams were monitored continuously and samples of concentrate and transite were taken for analytical determination of the content of free acid, lactate, nitrate and sodium ions in 1 hour interval.

Table 1 Streams feed in studied cases

	Diluate	Transite	Concentrate	Arrangement
1 case	1 l; 3 %wt HNO_3	0.6 l; 20 %wt LacNa	1 l; 2 %wt $NaNO_3$	CM-CM-AM
2 case	0.6 l; 20 %wt LacNa	1 l; 3 %wt HNO_3	1 l; 3 %wt LacH	CM-CM-AM
3 case	1 l; 3 %wt HNO_3	0.6 l; 20 %wt LacNa	1 l; 3 %wt LacH	CM-AM-AM
4 case	0.6 l; 20 %wt LacNa	1 l; 3 %wt HNO_3	1 l; 2 %wt $NaNO_3$	CM-AM-AM

Obtained results were evaluated using Eqs. (1)–(5), for the calculation of mass and molar fluxes (Eqs. (1), (2)), energy consumption (Eqs. (4), (5)) and electrical efficiency (Eq. (3)).

$$J_{neq(\mathbf{LacH})} = \frac{\Delta n_{(\mathbf{LacH})}}{\Delta t} \cdot \frac{1}{A \cdot N} \tag{1}$$

$$J_{meq(\mathbf{LacH})} = \frac{\Delta n_{(\mathbf{LacH})}}{\Delta t} \cdot \frac{M}{A \cdot N} \tag{2}$$

$$\eta = \frac{Q_{teor}}{Q_{skut}} = \frac{\Delta n_{(LacH)} \left| \nu \cdot z \right| \cdot F}{I \cdot N.t} \tag{3}$$

$$E_m = \frac{Q \cdot U}{m_{(\mathbf{LacH})}} = \frac{U \cdot I \cdot t}{m_{(\mathbf{LacH})}} \tag{4}$$

$$E_V = \frac{Q \cdot U}{V} = \frac{U \cdot I \cdot t}{V} \tag{5}$$

$J_{neq(LacH)}$ [mol.m^{-2}.h.$^{-1}$], $J_{meq(LacH)}$ [g.m^{-2}.h^{-1}] – molar and mass flux densities calculated from produced LacH quantity,
E_m [Wh.kg^{-1}] – specific energy consumption of pure lactic acid, E_V [Wh.l^{-1}] – specific energy consumption on product volume at reached concentration, $m_{(LacH)}$ [g] – product mass of
LacH, $n_{(LacH)}$ [mol] – product molar amount LacH, A [m^2]– active membrane area, N – number of membrane triplets,
Q [C] – electric charge, U [V]– voltage, F – Faraday constant 96485,3 C.mol^{-1}, ν – stoichiometry coefficient, z – ion charge, t [s]– time.

3 Results and discussion

Collected data of specific conductivity and pH are shown in Figs. 3–10 for all studied cases. Analytically determined lactic, free acid, nitrates and sodium ions concentrations are shown in Figs. 11–14. The power consumption and electrical efficiency were calculated from the acid concentration time difference, electric current and charge using Faraday law (Eq. (3)). Mass and molar flux densities (Eqs. (1), (2)) were derived from analytical determining of acid, sodium and nitrate ions content. Electric efficiency is ratio of real used electric charge and charge corresponding to performed mass transport.

In the 1st and 2nd case, the major pollutant is sodium ion, which was substituted by hydrogen ion. In case 1 and 2, free acid and sodium ion content are determined and their time dependences are shown in Figs. 11 and 12. The penetration of nitrates is assumed to be negligible in these arrangements. Different membrane arrangement in case 3 and 4 changes the testing conditions. Lactate and nitrate mixing occurs, so the nitrate ion is a major pollutant. Free acid and nitrate ion content was determined and shown in Figs. 13 and 14. In these cases strong hydrogen cation penetration occurs due to its high mobility (see Table 2) into all compartments.

Table 2 Diffusion coefficients of ions in water in infinite dilute in 25°C [13]

	D (10^{-9}) [m^2.s^{-1}]
H^+	9.311
Na^+	1.334
NO_3^-	1.902
Lac^-	1.033

In the first case (Fig. 2a) a conductivity drop in T which has its minimum in 125th minute is visible in Fig. 3. At the beginning was the conductivity of concentrate kept constant, nevertheless, after 125th minute it become to grow rapidly. The concentrate and transite pH curves (Fig. 5) went through inflective point in 125th minute. In Fig. 11 the change in slope of lactic acid content is observed in about the 125th min, but the slope of sodium ion content occurs break in 170th minute. In the 170 minute transite conductivity became stable at value of 15 mS.cm^{-1}. Due to lower lactic acid dissociation than sodium lactate dissociation, the conductivity minimum occurs at the limit salt transformation of lactate into lactic acid. As the membranes are not absolutely selective, nitrate ions penetration through CMs to the product stream occurs. Because the nitric acid is stronger than lactic acid, the reaction equilibrium incline to form sodium nitrate and lactic acid. After the formation of maximum possible amount of lactic acid in 125th minute, the conversion of sodium nitrate into nitric acid takes place. This fact corresponds to sodium ions removal, which is observable from its drops to minimum at about 170th minute. Then, the conductivity rises again due to the nitric acid formation. So by monitoring of pH and conductivity, the progress and degree of lactic acid formation process can be evaluated.

In the second case (Fig. 2b), nitric acid was fed into T, where the substitution of hydrogen by sodium cation on immobilized nitrate anion occurred. The conductivity of T periodically dropped due to loosing acid and its re-filling, see Fig. 4. The transite pH is low (Fig. 6) due to nitric acid content. The concentrate conductivity and pH increasing causes leakage of sodium ions through T and forming dissociative salts in concentrate. The nitrate ions leaking could also increase the conductivity, but its content was not determined, unfortunately. The weak increase of concentrate pH corresponds to analytical determination. Figure 12 shows the pollution of concentrate by alkali sodium ions.

The third tested case (Fig. 2c) using the arranging of two AMs as transit chamber is used for sodium cations retention. The low purity of the product is expected in this arrangement due to lactate low mobility and mixing with more mobile nitrate ions. The rapid growth of the C conductivity and decreasing of pH under 1.0 (Figs. 7, 9) marks out the nitrate ion penetration from T and its recombination into nitric acid. The pure lactic acid of molarity 1.3 mol.l^{-1} with pKa = 3.86 reaches the pH = 1.36, for the illustration. The analytical measurement showed in Fig. 13 confirms previous assessment. The first lactic acid content increasing in C is followed by high increasing of nitrate content thanks to nitrate ions leaking through transit stream.

The fourth case (Fig. 2d) was designed for substitution of nitrate anion by less movable lactate ion. The transit stream was designed to immobilize protons in transite stream. The transit's stream conductivity drop (Fig. 8) and pH increasing to the value about 2.0 (Fig. 10) marks out the conversion of the acid nitric acid into lactic acid in the 70th minute. This conversion corresponds with concentrate conductivity growth due to $NaNO_3$ inflow, so as the analytical measurement shows in Fig. 14. Concurrently the protons leaking through the membranes into other chambers occurs and decreases the final lactic acid concentration.

The rate of acid formation is expressed as lactic acid mass and molar flux through area unit of membrane triplet. In Table 3 the amount of produced acid, purity, concentration, and specific electric energy and nitric acid consumptions are compared. In accordance to Baily's [1] observing, the rate of lactic acid formation is driven by the slowest ion transport. So the highest reaction rate (equivalent mass flow) is reached in the 1st case thanks to transport of high mobility hydrogen and sodium cations. Also the highest lactic acid concentration has been reached with good purity. Drawback of this arrangement is the consumption of mineral acid due to hydrogen leaking into concentrate. The results of the 2nd and 3rd case show medium production rate and half acid consumption, but the purity of lactic acid is low. The 4th arrangement produced the lowest concentration of lactic acid of the highest purity. It has the highest demand on power consumption on product mass due to low electrical efficiency.

Table 3 Comparsion of the results of the 4 cases after 4.5 hour test

	AM-CM-CM		**AM-AM-CM**	
	1 case	**2 case**	**3 case**	**4 case**
Jn eq (LacH) [mol.m^{-2}.h^{-1}]	**10.9**	**3.7**	**3.9**	**0.707**
Jm eq (LacH) [g.m^{-2}.h^{-1}]	982	330	350	64
Em (LacH) [Wh.kg^{-1}]	585	646	395	4864
Ev (LacH) [Wh.l^{-1}]	136	81	51	135
Electrical efficiency	74%	81%	73%	18%
End-test reached values:				
c LacH [g.l-1]	**223**	**89**	**86**	**31**
purity LacH [% wt]	98.95 %	95.82 %	40.50 %	99.38 %
purity LacH [% wt]	99.16 %	85.40 %	31.91 %	99.38 %
consumption HNO_3 [kg.l^{-1}]	0.421	0.200	0.129	0.060

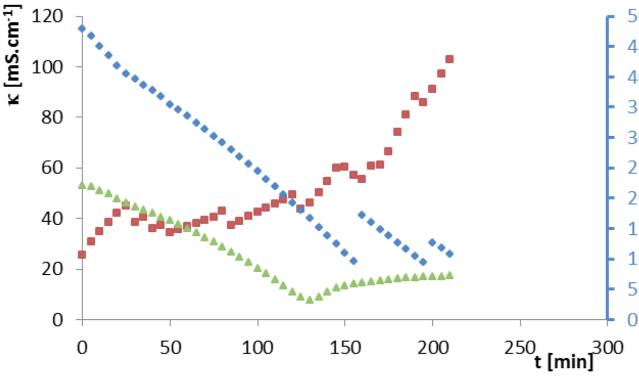

Fig. 3 Case 1, specific conductivities progress: ♦ D, ■ C, ▲ T

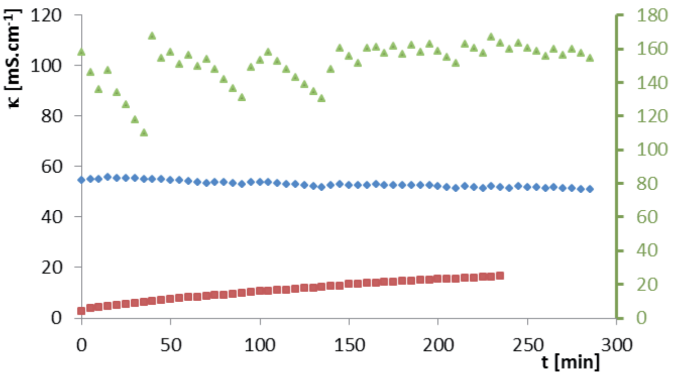

Fig. 4 Case 2, specific conductivities progress: ♦ D, ■ C, ▲ T

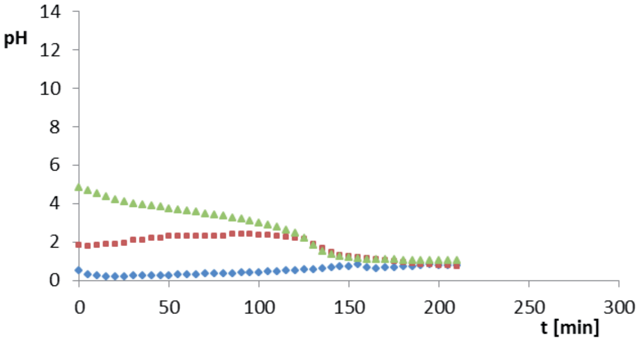

Fig. 5 Case 1, pH progress: ♦ D, ■ C, ▲ T

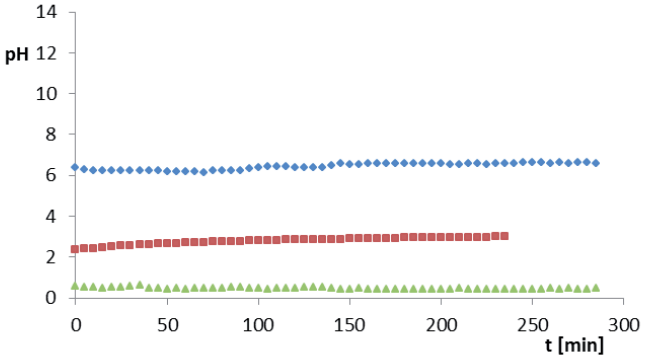

Fig. 6 Case 2, pH progress: ♦ D, ■ C, ▲ T

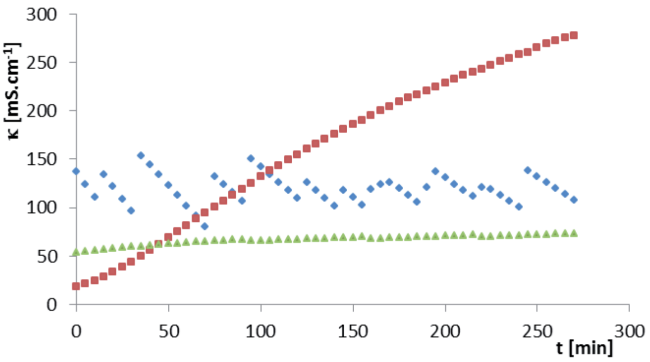

Fig. 7 Case 3, specific conductivity progress: ◆ D, ■ C, ▲ T

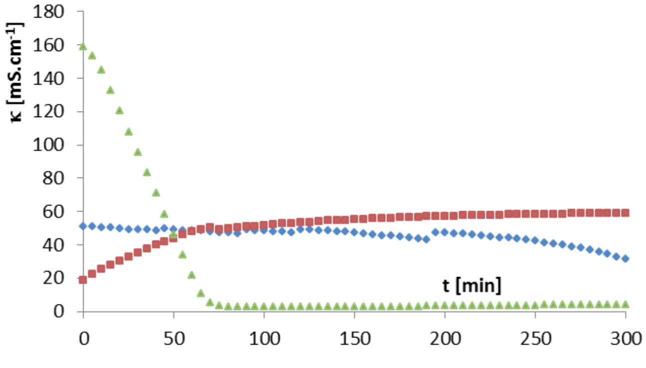

Fig. 8 Case 4, specific conductivity progress: ◆ D, ■ C, ▲ T

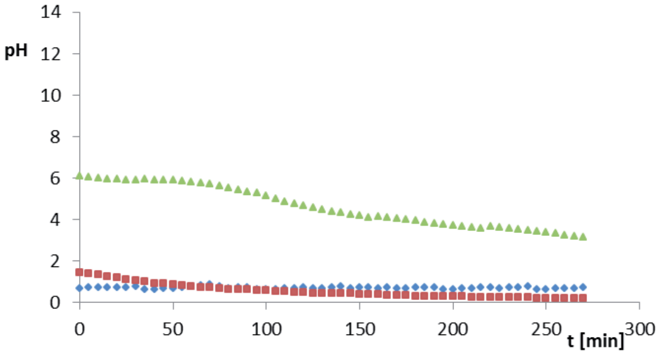

Fig. 9 Case 3, pH progress: ◆ D, ■ C, ▲ T

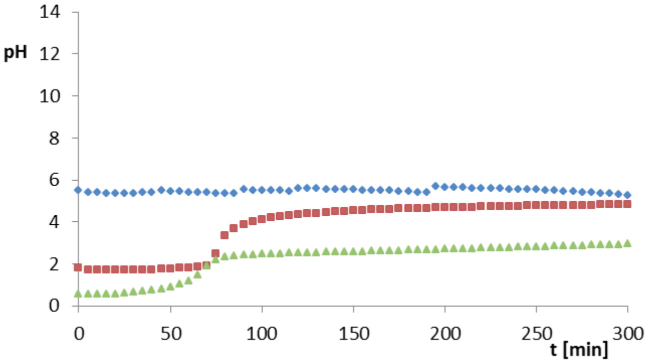

Fig. 10 Case 4, pH progress: ◆ D, ■ C, ▲ T

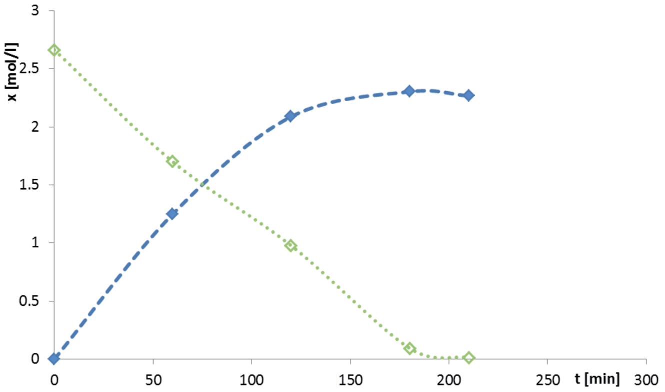

Fig. 11 Product molar concentrations in case 1 (T): ♦ lactic acid, □ sodium ion

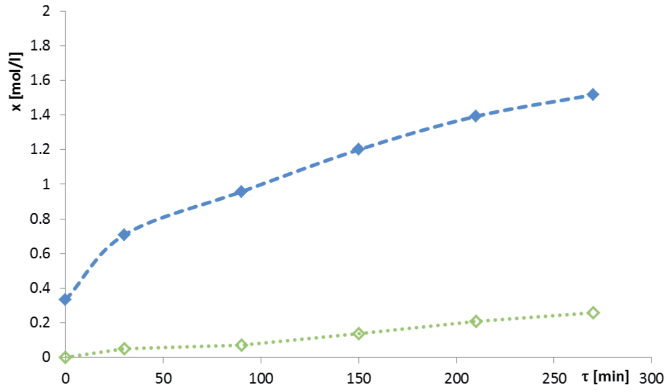

Fig. 12 Product molar concentration in case 2 (C): ♦ lactic acid, □ sodium ion

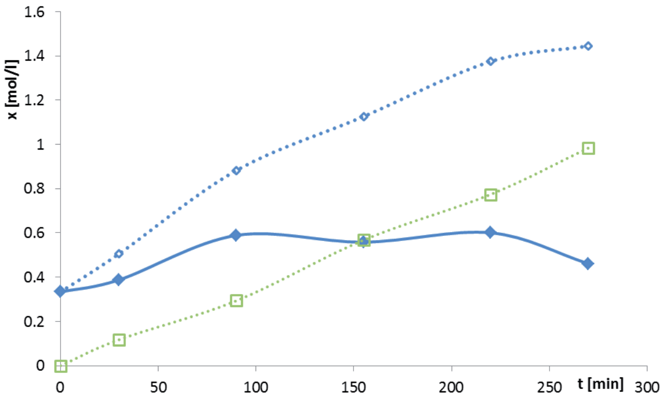

Fig. 13 Product molar concentration in case 3 (C):
◊ free acid, ♦ lactic acid, □ nitrate ion

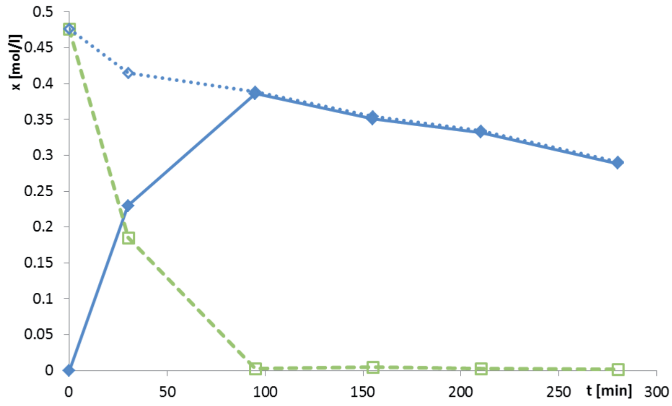

Fig. 14 Product molar concentration in case 4 (T):
◊ free acid, ♦ lactic acid, □ nitrate ion

4 Conclusions

Comparing the collected data (Table 3) results the conclusion that this method is applicable to produce large-anion organic acids from their salts. The 1st case arrangement appears to be the most suitable solution, which produces the most concentrated lactic acid with relatively high efficiency. The equilibrium point in weak acid production is easily recognized as conductivity minimum and pH inflection. The drawback is the need of mineral acid as protons source.

The 4th case arrangement produces the lactic acid of higher purity than the 1st case arrangement, as well consumes the lower amount of inorganic acid. On the other side the 4th case product is lower concentrated than that of the 1st one, and its process could not operate in continous mode.

The limitation of producing the high purity chemicals is pollution by ions penetrated the membranes due to non-ideal selectivity from neighboring chambers. The condition of this ED-S method is that the dissociation constant of the product should be lower than that of its precursor salt.

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References

[1] Bailly, M., Roux-de B., Lutin, F., Aimar, P., Cheryan, M. "Production processes of fermented organic acids targeted around membrane operations: design of the concentration step by conventional electrodialysis." *Journal of Membrane Science*. 191 (1-2). pp. 129-142. 2001. DOI: 10.1016/S0376-7388(01)00459-8

[2] Bjornsdottir, K., Breidt, F. Jr. "Protective Effects of Organic Acids on Survival of Escherichia coli O157:H7 in Acidic Environments." *Applied and Environemntal Microbiology*. 72 (1). pp. 660-664. 2006. DOI: 10.1128/AEM.72.1.660-664.2006

[3] Boniardi, N., Rota, R., Nano, G., Mazza, B. "Lactic acid production by electrodialysis Part I: Experimental tests." *Journal of Applied Electrochemistry*. 27. pp. 125-133. 1997. DOI: 10.1023/A:1018439604632

[4] Buenaventurada, P. C., Ninomiya, Funabashi, M., Hisaaki, Y., Oishi, A., Taguchi, K., Kunioka, M. "Biodegradable Poly(butylene succinate) Composites Reinforced by Cotton Fiber with Silane Coupling Agent." *Polymers*. 5 (1). pp. 128-131. 2013. DOI: 10.3390/polym5010128

[5] Fakhravar, S., Najafpour, G., Heris, S. "Fermentative Lactic Acid from Deproteinized Whey Using Lactobacillus bulgaricus in Batch Culture." *World Applied Science Journal*. 17 (9). pp. 1083-1086. 2012.

[6] González, M. I., Alvarez, S., Riera, F. A., Álvarez, R. "Lactic acid recovery from whey ultrafiltrate fermentation broths and artificial solution by nanofiltration." *Desalination*. 228. pp. 84-96. 2008. DOI: 10.1016/j.desal.2007.08.009

[7] Hábová, V., Melzoch, K., Mejta, V., Rychtera, M., Přibyl, L. "Application of electrodialysis for lactic acid recovery." *Czech Journal of Food Sciences*. 19 (2). pp. 73-80. 2001.

[8] Heriban, V., Škára, J.,Šturdík, E., Ilavský, J. "Isolation of free lactic acid using electrodialysis." *Biotechnology Techniques*. 7 (1). pp. 63-68. 1993. DOI: 10.1007/BF00151092

[9] Heriban, V., Šturdík, E. "*Fermentačná Produkcia kyseliny mliečnej. Kvasny prum*." 11. pp. 328-331. 1989.

[10] Hsiao, H.-Y., Walter, J. F., Anderson, D. M., Hamilton, B. K. "Enzymatic production of amino acids." *Biotechnology and Genetic Engineering Reviews*. 6 (1). pp. 197-220. 1988. DOI: 10.1080/02648725.1988.10647848

[11] Huang, Ch., Xu, T., Zhang, Y. "Application of electrodialysis to the production of organic acids: State-of-the-art and recent developments." *Journal of Membrane Science*. 288 (1-2). pp. 1-12. 2007. DOI:10.1016/j.memsci.2006.11.026

[12] Kangwanwatthanasiri, P., Suppakarn, N., Ruksakulpiwat, Ch., Ruksakulpiwat, Y. "Biocomposites From Cassava Pulp / Polylactic acid / Poly(butylene succinate)." *Advanced Materials Research*. 747. pp. 367-310. 2013. DOI:10.4028/www.scientific.net/AMR.747.367

[13] Mohr, P. J., Taylor, B. N., Newell, D. B. "CODATA recommended values of the fundamental physical constants: 2010." *Reviews of Modern Physics*. 84. 2012. DOI: 10.1103/RevModPhys.84.1527

[14] Narayanan, N., Roychoudhury, P. K., Srivastava, A. "L(+) lactic acid fermentation and its product polymerization." *Electronic Journal of Biotechnology*. 7 (2). 2004. DOI: 10.2225/vol7-issue2-fulltext-7

[15] Omar, F. N., Rahman, N' A. A., Hafid, H. S. "Separation and recovery of organic acids from fermented kitchen waste by an integrated process." *African Journal of Biotechnology*. 8 (21). pp. 5807-5813. 2009.

[16] Raj, S. M., Rathnasingh, Ch., Jo. J-E., Park, S. "Production of 3-hydroxypropionic acid from glycerol by a novel recombinant Escherichia coli BL21 strain." *Process Biochemistry*. 43. pp. 1440-1446. 2008. DOI: 10.1016/j.procbio.2008.04.027

[17] Solti, K. "Synthesis and characterization of poly(aspartic acid) / poly(N) isopropylacrylamide conetwork hydrogels. in: Conference of MSc Students Abstracts of the best contributions." *Periodica Polytechnica Chemical Engineering*. 57 (1-2). pp. 106-107. 2013. DOI: 10.3311/PPch.2178

[18] Theron, M. M., Lues, J. F. R. "*Organic Acids and Food Preservation*." New York: Taylor & Francis. 2011. ISBN: 978-1-4200-7843-5

[19] Vandenberghe, L. P. S., Soccol, C. R., Pandey, A., Lebault, J.-M. "Microbial production of citric acid." *Brazilian Archives of Biology and Technology.* 42 (3). 1999.

[20] Vroman, I., Tighzert, L. "Biodegradable polymers." *Materials.* 2 (2). pp. 307-344. 2009. DOI:10.3390/ma2020307

[21] Xinlin, J., Qianzhu, L., *Journal of Chemical and Pharmaceutical Research*. 6 (5). pp. 374-381. 2014.