Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Fermentation Products by Membrane Techniques. II. Conversion of Lactate to Lactic Acid by Electrodialysis

Anna Narebska; Małgorzata Kurantowicz

To cite this Article Narebska, Anna and Kurantowicz, Małgorzata(1998) 'Separation of Fermentation Products by Membrane Techniques. II. Conversion of Lactate to Lactic Acid by Electrodialysis', Separation Science and Technology, 33: 7, 959 — 973

To link to this Article: DOI: 10.1080/01496399808545001

URL: http://dx.doi.org/10.1080/01496399808545001

SEPARATION SCIENCE AND TECHNOLOGY, 33(7), pp. 959–973, 1998

Separation of Fermentation Products by Membrane Techniques. II. Conversion of Lactate to Lactic Acid by Electrodialysis

ANNA NARĘBSKA* and MAŁGORZATA KURANTOWICZ
FACULTY OF CHEMISTRY
NICOLAUS COPERNICUS UNIVERSITY
UL. GAGARINA 7, 87–100 TORUŃ, POLAND

ABSTRACT

The yield of an electrodialysis unit operating for the conversion of lactate to lactic acid (LA) is depressed by low conductivity of the lactic acid solution. Experiments performed with a laboratory electrodialysis unit (ED) designed to establish the limiting current density $i_{\lim}$ for the whole unit and for each of the membrane/solution elements revealed high voltage drops for membranes in contact with the lactic acid solution. By filling the LA compartment with a cation-exchange resin as the conducting turbulence promoter, it was possible to increase $i_{\lim}$ from 2.7 ± 0.3 to 18.3 ± 2.0 mA/cm^2. With a resin suspension the rate of lactic acid formation was 6.0 mol·m^{-2}·h^{-1}, the current efficiency amounted to 92%, and the energy consumption was 3.3 kW·h·kg^{-1}. A hypothesis for the ~7-fold increase of $i_{\lim}$ by filling the LA compartment with a grained conducting resin is presented.

INTRODUCTION

The production of carboxylic acids by the bacterial fermentation of carbohydrates is practised on an industrial scale. The progress in fermentation technology achieved in the 1950s and 1960s imposed the selection of the process configurations to the microorganisms and the substrates: lactose, glucose, saccharose, etc. Another part of the process, the recovery of the final products from broths, still requires new techniques. Several processes were

---

* To whom correspondence should be addressed.

developed for the isolation of free, possibly concentrated acids from broths. Some of them have not been disclosed (1).

For the isolation of products it is important that most of bacteria tolerate pH from ~4 to 8 with the maximum rate of cell growth and productivity in the 5.5–6.5 range. The optimum pH is strain-dependent. To keep the optimum pH, broth is neutralized by calcium carbonate or hydroxides. Thus carboxylates are the main products in the neutralized broth. After recovery, the products are processed further. If lactic acid is intended as the final product, the conversion of carboxylate to carboxylic acid should be the next step in the operation.

In an early conventional technology with calcium carbonate as the neutralization agent, the isolated calcium carboxylate was concentrated and treated with sulfuric acid to produce carboxylic acid. The successive filtration, bleaching, evaporation, and formation of calcium sulfate as the waste made the technology laborious and ineffective. Other examined processes were crystallisation, liquid–liquid extraction, and esterification followed by hydrolysis.

Beginning in the 1970s, but mainly in the 1980s and 1990s, electrodialysis has been tested as a technique for treating fermentation products, mostly for the production of lactic acid. The purposes for integrating electrodialysis (ED) with fermentation were different. ED can be used for the desalination of substrates (2–4), for the recovery of lactates (5–7), for the conversion of lactate to lactic acid, and for the one-step conversion and concentration of the acid (8, 9). Also, the proposed ED units were different, starting from one membrane system (10) or simple four or five compartment units up to a multicomponent stack for operation on a large scale (11–13). A more complex system for the semicontinuous production of lactic acid by cells entrapped within the polymeric matrices, forming a fermenter joint to ED for the continuous recovery of the acid, has been modeled and examined by experiments (14).

The main conclusion is that periodic or continuous isolation of the fermentation products from broths by ED improves process efficiency.

Economy requires each electrodialysis unit to operate at the maximum allowable current density, yet below the polarization limit. In practice, this means the current density ranges up to 75–80% of the limiting current. Above the limiting current (I_{lim}) the water molecules ionize (i.e., "split"), consuming energy unprofitably and changing the pH of the feed and/or the concentrate. Concentration polarization is a well known phenomenon studied thoroughly for both its fundamentals and practical implications. Many papers have been published, but only a few relating to the problem will be quoted (15–21).

The limiting current density (i_{lim}) is not easy to determine for electrodialysis units operating for desalination. It is even more difficult to establish i_{lim}

for a system containing different solutes in each compartment and with one of the compartments filled with a solution whose conductivity is below the conductivity of the membranes.

This paper focuses on establishing the limiting current density for the four-compartment electrodialysis unit (two operating and two terminal) used for the conversion of sodium lactate (NaLA) to lactic acid (LA).

The experiments were carried out with model solutions containing sodium lactate of the concentration which corresponded to the concentration in a broth produced by fermentation of glucose by *Lactobacillus delbrueckii.*

ELECTRODIALYSIS UNIT FOR THE SALT-TO-ACID CONVERSION. AN ARRANGEMENT AND PROBLEMS

The conversion of salt to acid with the use of electrodialysis is simple as an idea. In the four-compartment unit, the ultrafiltered broth is let into a compartment with an anion-exchange membrane on the anode side and a cation-exchange membrane on the cathode side (Fig. 1). Lactate ions migrate in the constant electric field across the anion-exchange membrane to the neighboring compartment (here Compartment 3). At the same time, hydrogen ions migrate to the same compartment from the anode solution through the cation-exchange membrane. Thus, the acid is formed one-to-one to the lactate ions recovered from a broth. This is a theoretical limit. This process takes place in an electrodialyzer with unipolar membranes. If an ED unit containing a bipolar membrane is used instead of the cation-exchange membrane (on the anode side), the hydrogen ions are formed directly in Compartment 3.

In this paper we focus on electrodialysis with monopolar membranes. The overall arrangement of the unit and the contents of the compartments are seen in Fig. 1. Each of the three membranes in the unit may affect the current density by concentration polarization, but not to the same extent. Another effect which limits the current is the low conductivity of the compartment filled with lactic acid. A short analysis of conduction in the unit leads to the following.

In *Compartments 1/2* with a cation-exchange membrane separating the cathode solution and the broth (Fig. 1b), sodium ions migrate from the broth toward the cathode compartment. Concentration polarization should not affect the current until the broth is depleted of lactate. The conductivities of both of solutions are relatively high, and they exceed the membrane conductivity.

In *Compartments 2/3* with an anion-exchange membrane separating the broth and lactic acid solution (Fig. 1c, c′), lactate ions migrate from the broth toward Compartment 3. Concentration polarization on the feed side depends on the concentration of the broth. If the surface layer is depleted of LA^- ions, water molecules split, producing OH^- ions which migrate across the

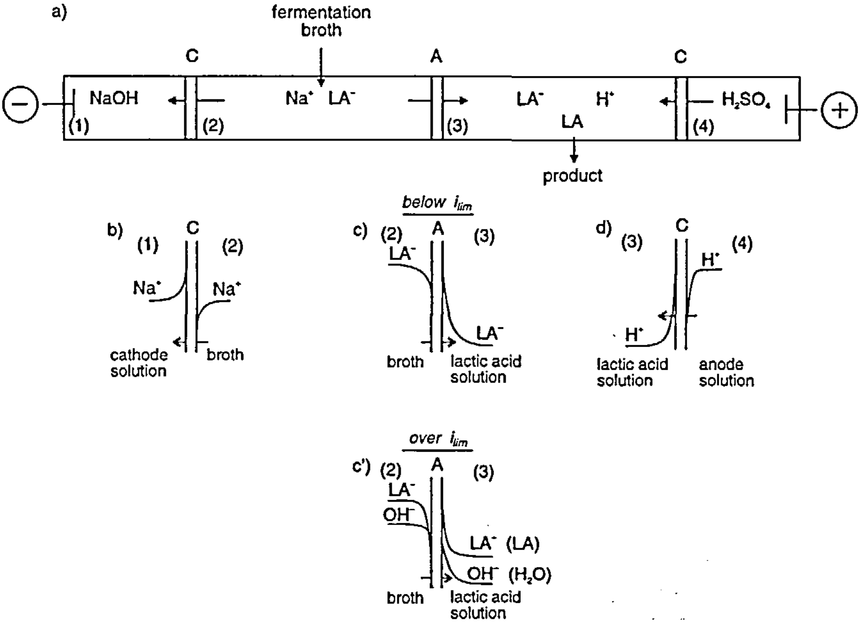

FIG. 1 Schemes for lactate to lactic acid conversion in the four compartment ED unit (a) and the polarization phenomena on membranes (b–d). Membranes: A = anion exchange (here Neosepta AM-1, Tokuyama Corp., Japan); C = cation exchange (Neosepta CM-2). Solutions: cathode = 0.2 mol/L NaOH; model solution for broth = sodium lactate (NaLA), C_{NaLA} = 0.25 mol/L; product = starting solution of lactic acid (LA), c_{LA} = 0.1 mol/L; anode = 0.1 mol/L. H_2SO_4 + 0.05 mol/L Na_2SO_4.

membrane. On the opposite side of this membrane, the concentration of ions is low because of the nature of the acid formed. This seems to be the weakest part of the unit.

In *Compartments 3/4* with a cation-exchange membrane separating lactic acid and the anode compartment (Fig. 1d), hydrogen ions migrate from the anode compartment to Compartment 3 where lactic acid is formed. The transport number of hydrogen ions in the membrane is close to unity up to the concentration of sulfuric acid; ~1 mol/L. To protect the surface layer of the membrane from depletion of ions, some amount of sodium sulfate could be added. Again, the conductivity of the anode solution is high whereas it is low on the opposite side of the membrane.

The equipment used for estimating potential drops on each membrane/solution element and the experimental results are discussed in the following sections.

EXPERIMENTAL

Electrodialysis Unit

The main differences between the ED unit designed here and standard laboratory units for desalination are the number of electrodes and the intermembrane spaces. Apart from the platinum terminal electrodes, more Pt wire probe electrodes were localized on both sides of each membrane close to the surface (two terminal + six probe electrodes). In order to measure undisturbed potential drops, the intermembrane distance in Compartments 2 and 3 was 20 mm each. In this configuration the measured voltage drop encompassed by the drop on a membrane and the layer of solution exceeds the stagnant boundary layer. The voltage drop was measured in one passage for the whole unit and the three membrane/solution elements. The experimental setup is seen in Fig. 2.

Current was supplied by a ZT-980-4M power unit (Unitra, Poland) and checked with a digital multimeter (Metex M4650, Poland). Three additional digital multimeters measured the potential drop for each element. Solutions

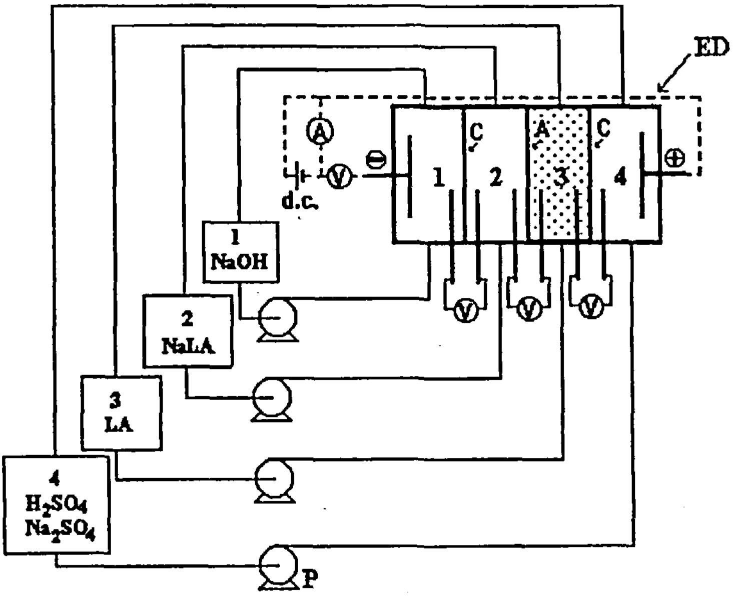

FIG. 2 Laboratory experimental setup. ED = four compartment electrodialysis unit with the cation (C) and anion (A) exchange membranes. P = peristaltic pump. A = ammeter. V = voltmeter.

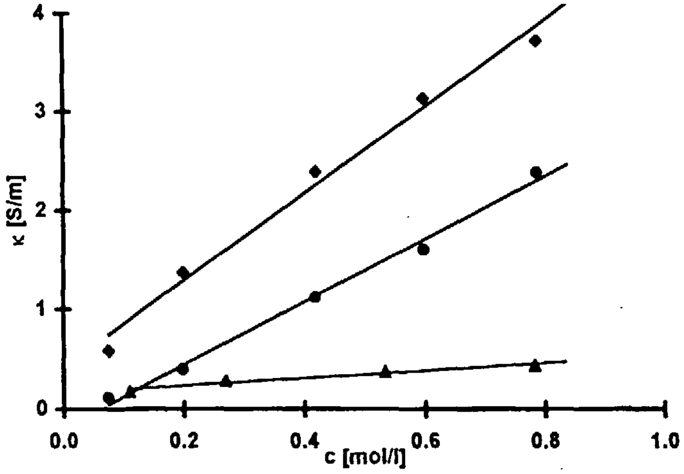

FIG. 3 Specific conductivity of sodium lactate (◆), lactic acid (▲), and Neosepta AM-1 in contact with sodium lactate (●).

were pumped with a MasterFlex pump (USA) at the rate of 100 mL/min for each compartment. The surface of each membrane was 12.56 cm^2. Experiments were carried out at 298 K (air thermostat).

After establishing the critical current densities, experiments on the salt-to-acid conversion were carried out for 5 hours and for up to 1 week. These experiments enabled a detailed examination of mass transfer and the computation of energy consumption per unit of a product to be made. Another goal, particularly for the long experiments, was to establish the maximum possible concentration of the acid at a reasonable energy consumption of the system.

Some additional experiments were performed using a FuMA-Tech electrodialyzer TS001 (FuMA-Tech, Germany).

The conductivities of the solutions (LA and NaLA) and of the anion-exchange membrane in a solution of sodium lactate (Fig. 3) were determined using the RLC-bridge (Meratronik E318, Poland). The specific conductivity of the membrane was calculated by subtracting the conductance of the electrolyte from the conductivity measured for the cell with the membrane and electrolyte.

Membranes

Cation-exchange membrane Neosepta CM-2 and anion-exchange membrane Neosepta AM-1 (Tokuyama Corp., Japan) were used for experiments.

The membranes were prepared in the hydrogen form (CM-2) and in the lactate form (AM-1) by a repeated exchange in sulfuric acid and sodium lactate solutions. The characteristics of the membranes as determined by standard methods (29) are displayed in Table 1.

Chemicals

The molarities of sodium lactate (Sigma Chemical Co., USA) were from 0.1 up to 1.0; that is, the concentrations were higher and lower than the concentrations observed in the broths. In all experiments the starting concentration of lactic acid (POCh, Poland) was 0.1 mol/L. Sodium hydroxide (POCh, Poland) of 0.2 M and the bicomponent solution of sulfuric acid and sodium sulfate (POCh, Poland) of 0.1 + 0.05 M were used as the cathode and anode solutions, respectively.

Analytics

The concentration of lactic acid and sodium lactate (total) was determined by capillary electrophoresis (CS Capillary Electrophoresis Analizer EA 100, Villa Labeco, Slovakia). The accuracy in determining LA and NaLA was ±4%.

To follow lactic acid formation, the concentration of LA was determined after each 60 minutes in the 5-hour experiments and 120 minutes in the long time electrodialysis.

RESULTS AND DISCUSSION

Limiting Currents with Lactic Acid Solution in the Unit

A few methods for determining the limiting current density are known (15–21). For a unit and experiments such as ours, the Cowan method seemed

TABLE 1
Characteristics of the Neosepta Membranes

Properties	Neosepta AM-1[a]	Neosepta CM-2[b]
Ion-exchange capacity (mmol/g)	1.74	1.63
Water content (g/g)	0.24	0.25
Electrical resistance ($\Omega\cdot cm^2$)	1.22	2.12
Thickness (cm)	0.012	0.014

[a] Cl-form.
[b] Na-form.

appropriate (22). For the unit and each membrane/solution elements, the resistance ($R = V/I$) was drawn against the reciprocity of current ($1/I$). The resistance drops linearly while the current increases until the stagnant layers on the membrane surfaces become depleted of ions from the bulk. This is the point at which the resistance increases sharply Fig. 4. The point of intersection

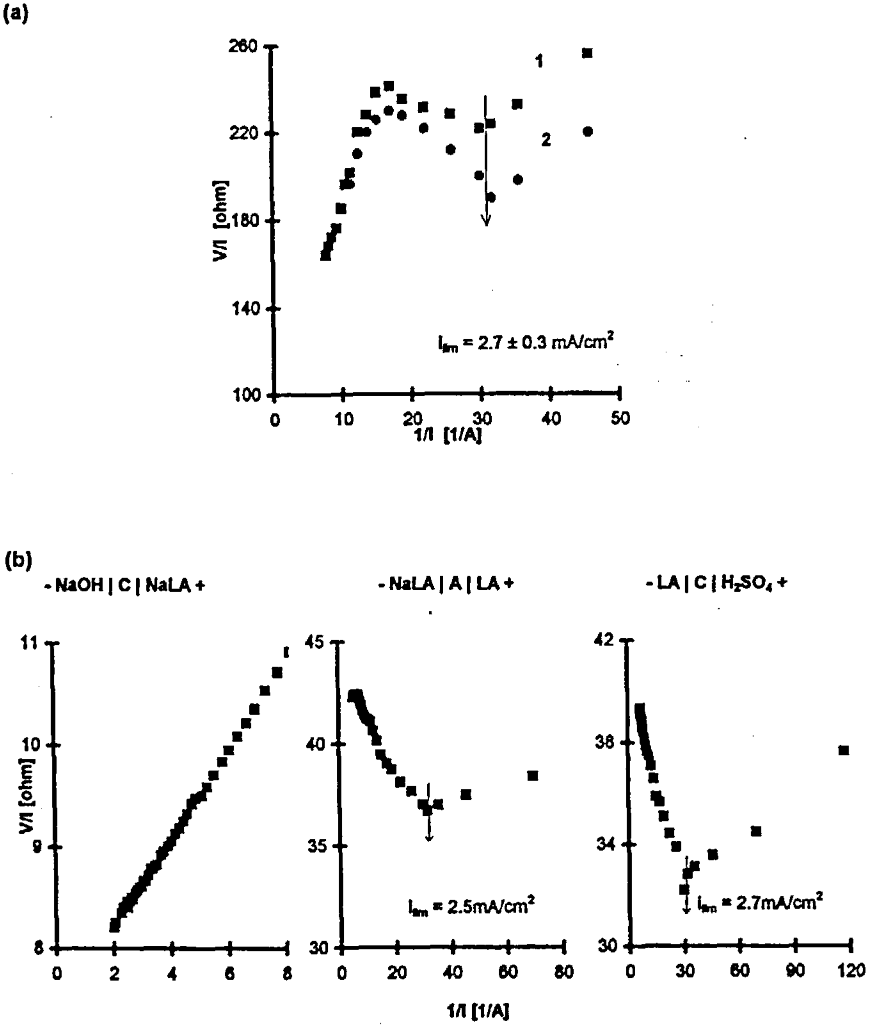

FIG. 4 Cowan plots for electrodialysis unit (a) and the constituting membrane/solution elements (b). (1) Whole unit; (2) the unit without the potential drop on terminal electrodes.

of the downward and upward sections of a curve indicates the limiting current value. Because of deviations from linearity in the slopes, determination of the limiting current density cannot be precise. From our experience, the inaccuracy is in the range from ±0.3 mA (low current) up to ±2.0 mA (high current).

Because of the arrangement of the unit, the total potential drop is the sum of the electrode potential (V_e), the concentration potential (V_c), the polarization voltage (V_p), and the ohmic resistances R (22):

$$V/I = R + (V_e + V_c + V_p)/I \tag{1}$$

Each plot additionally provides the ohmic resistance of the unit (by extrapolating the downward slop to the y-axis) and the resistance at the point of intersection (V_p/I), i.e., just before a sharp polarization starts. By measuring the potential drops between the electrodes in the terminal compartments (Fig. 2), it was possible to subtract the electrode potential V_e, thus reducing the number of variables in Eq. (1).

Figure 4 presents Cowan plots for the whole electrodialysis unit with lactic acid solution in Compartment 3 (upper plot, Curve 1). Curve 2 is for the same unit but with the terminal electrodes potential subtracted. The three plots at the bottom of Fig. 4 are for separate membrane/solutions elements.

From Curves 1 and 2 (Fig. 4) it appears that the limiting current density for the whole unit is as low as 2.7 ± 0.3 mA/cm^2. On the cation-exchange membrane with adjoining cathode and feed solutions, an increase of current does not result in the limitations up to quite as high a current (for more details see Fig. 5). It is not the same, however, for the two other membrane/solution elements. For these, the resistances at the inflection points are 36.5 and 32.5 Ω, and both exert limitations on the current.

Because of the low current density (2.7 mA/cm^2), the flux of LA$^-$, and consequently the rate of lactic acid formation, was ~2 mol·m^{-2}·h^{-1} whereas the current efficiency for conversion was as low as 25%.

Limiting Current with the Ion-Conducting Filler in the Lactic Acid Compartment

Strong acid cation-exchange resin in the hydrogen form was used to increase the conductivity of the compartment filled with lactic acid solution. Resin beads in the form of a fluidized bed of high resin content were entrapped in the intermembrane space of Compartment 3.

Spacers for electrodialyzers are usually made of inert materials, but the use of conducting spacers is not a new idea. In 1976 Kedem and Maoz (23) reported using a spacer made of cation and anion fibers knitted separately and put together to form a 2.5-mm thick bilayer spacer. The current density

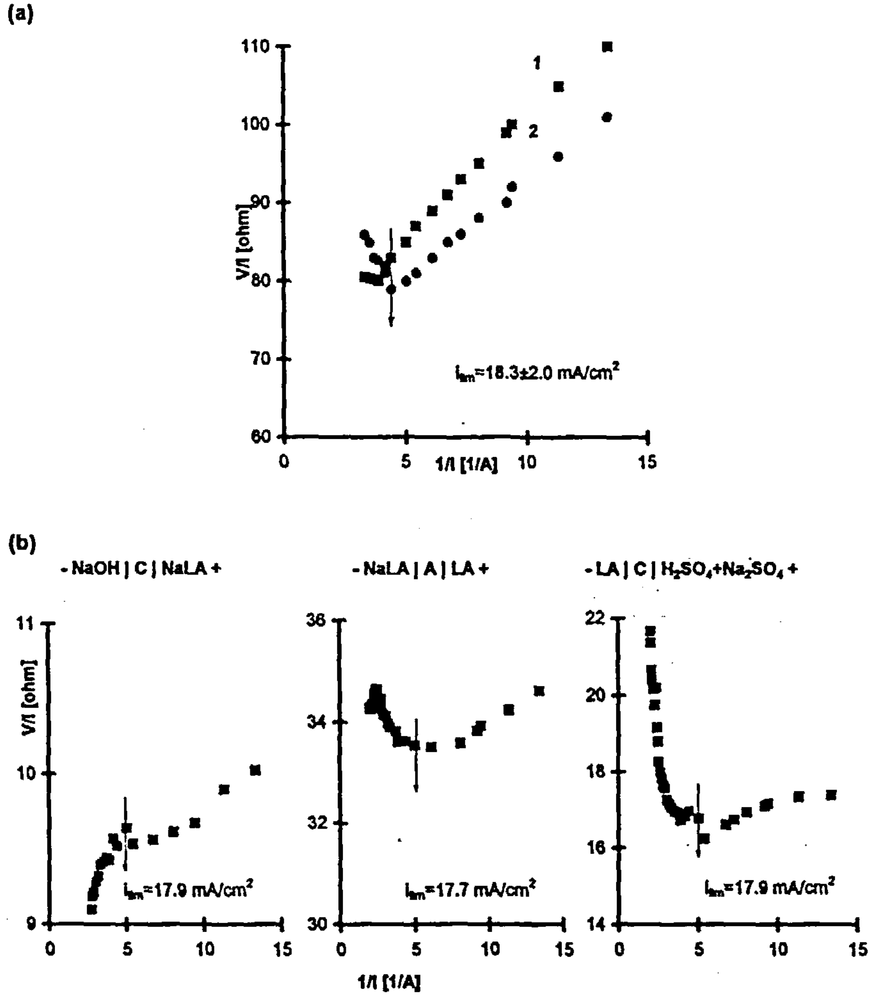

FIG. 5 Cowan plots for electrodialysis unit with the suspension of resin in lactic acid compartment (a) and the constituting membrane/solution elements (b). (1) Whole unit; (2) the unit without the potential drop on terminal electrodes.

with this spacer was found to be twice as high as with an inert spacer of the same shape. In 1955 Walters et al. (24) used mixed-bed cation and anion granular exchange resins to fill the deionization compartment in a multimembrane cell while treating radioactive aqueous wastes. The purpose of using a mixed resin bed was to remove traces of radioactive metal ions by ion exchange while maintaining the current density at a level of 10 mA/cm^2, even in extremely dilute solutions.

In 1994 Stankovič (25) reported on the effect of granular turbulence promoters of different shapes made of inert material, on mass transfer enhancement and specific energy consumption in electrochemical processes. The author examined beds composed of fixed beads, fluidized beads, and packed cylinders, and he found a bed of fixed beads to be the most effective for increasing current. The intensification factor found amounted to 12.

In order to increase the current density in the ED unit for conversion, we tested two ion-exchange resins: Amberlite IR-120PLUS (Rohm and Haas Co., USA) and Dowex 50W (Dow Chemical Co., USA). As a result of the experiments, the Amberlite resin of mesh size 16–50 was selected. The AC resistance of lactic acid (c = 0.1 mol/L) and the dense suspension of resin in lactic acid are 4.92 Ω·m for the acid and 1.85 Ω·m for the suspension of Amberlite IR-120PLUS in the acid.

Figure 5 presents Cowan plots for the same unit as reported in Fig. 4 with the suspension in Compartment 3. The limiting current density is now 18.3 ± 2.0 mA/cm^2. The intensification factor, which denotes the ratio of the limiting current with and without the resin, is ~7. The effect is evident.

A more detailed analysis of the Cowan plots in Fig. 5 confirms a decrease of the overall resistance of the unit. For the cation-exchange membrane which separates the compartment filled with suspension from the anode compartment, the resistance is now half of that without the resin. In the following section we offer a hypothesis for the sevenfold increase of the limiting current density with resin as a conducting filler.

Hypothesis Concerning the Effect of a Grained Conducting Filler on Current Density

When using a grained filler, the observed increase in i_{lim} may be the result of promoting a turbulent flow (1), narrowing the solution layer in the intermembrane space (2), or active participation of a filler in mass transfer (3).

1. With the equipment used here (a glass cell with fastened probe electrodes and a Masterflex pump), the flow rate limit was from 100 to 480 mL/min. At these rates the flow is laminar. With an increase in the flow rate to the maximum possible for the pump, but still not disturbing the performance of the unit, the increases of the observed limiting current density were:

Flow rate:	100 mL/min, 0.24 cm/s	200 mL/min, 0.48 cm/s	300 mL/min, 0.72 cm/s
i_{lim} without the suspension:	2.7 mA/cm^2	3.8 mA/cm^2	4.2 mA/cm^2
i_{lim} with the suspension:	18.3 mA/cm^2	19.2 mA/cm^2	19.8 mA/cm^2

To measure an increase in $i_{\rm lim}$ at a still higher flow rate, experiments on the conversion of lactate were performed using a FuMA-Tech electrodialysis unit [$S_{\rm membrane} = 50\ {\rm cm}^2$, flow rate = 10 cm/s (1667 mL/min), calculated Reynolds number = 1700]. The membranes and solutions were the same as in the experiments displayed in Fig. 4. The limiting current density found in this unit was 12.2 mA/cm^2 (no conducting filler). Considering the figures, the current density is still below the limit found with the filler acting as the conducting turbulence promoter at a very low flow rate. Ways of saving energy in electrochemical processes, in units containing effective spacers, has been discussed by Chiapello et al. (26).

2. Due to the volume occupied by beads, the effective thickness of the solution in the compartment with the resin is smaller. For random close spheres, the packing factor amounts to 0.64. The volume of solution in the suspension is thus decreased to 0.36 of the total, and the solution layer to 7.2 mm. The layer is certainly still too thick to expect an observed effect in $i_{\rm lim}$. This model will possibly suit a bed formed by conducting liquids with suspended inert beads, but not here.
3. Only counterions are mobile in the resin. The resin was prepared with hydrogen counterions to fill the ED compartment. Thus, we postulate that the resin participates in conducting current by hydrogen ions which migrate from the cation-exchange membrane side across the suspension toward the anion-exchange membrane, where the lactic acid is formed (with LA^- ions crossing the membrane). Thus, the thickness of the solution were the acid forms is limited to a thin layer at the surface on the anion-exchange membrane.

If this hypothesis is correct, the percolation theory would be applicable for describing the transport of hydrogen ions across the suspension (27, 28). For three-dimensional space, the critical volume fraction of conducting spheres in which the infinite cluster forms is in the range of 0.303 (at most). For a suspension of beads like the one described here, this means that in order to enhance the current, it would be sufficient if the volume fraction occupied by the beads were in the range of the threshold volume, that is, about 0.3–0.4.

The increase of $i_{\rm lim}$ with a conducting spacer suspended in lactic acid solution is an effect of practical importance. Any other spacer, including a sheet-type spacer, conducting hydrogen ions and promoting turbulence would be helpful.

Current Efficiency and Energy Consumption in Lactate-to-Lactic Acid Conversion

The results of electrodialysis carried out at a current density of 18.3 mA/cm^2 and the suspension of resin in lactic acid solution are seen in Fig. 6. The

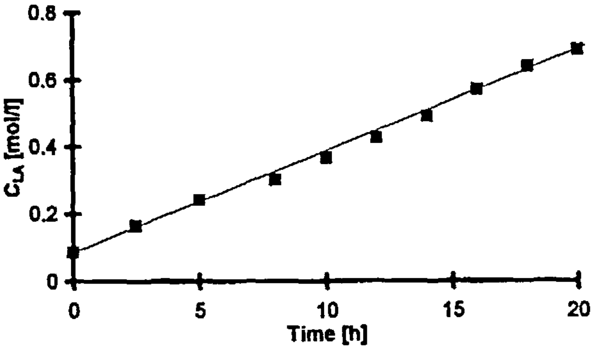

FIG. 6 Production of lactic acid in ED unit.

formation of lactic acid is linear until $c_{LA} = 0.7$ mol/L when the lactate flux is 6.0 mol·m^{-2}·h^{-1}. At longer times the curve declines to the x-axis.

The current efficiency for the process,

$$\eta = \frac{(c_0 - c_t)vF}{It} \times 100\% \tag{2}$$

and energy consumption for the acid production,

$$\eta_{EC} = \frac{tI\Delta V}{m} \tag{3}$$

are collected in Table 2.

The symbols used in Eqs. (2) and (3) have the following meanings: t = time (s), c_0 = concentration of LA at $t = 0$ (mol/L), c_t = concentration of LA in time t (mol/L), I = current (A), F = Faraday's constant (mol/C), v = volume of solution (L), m = mass of LA (kg), ΔV = potential difference (V).

TABLE 2
Productivity of ED Unit Applied for Lactate to Lactic Acid Conversion

	c^* (mol/L)[a]	J (mol/m^2·h)	η (%)	η_{EC} (kW·h/kg)
Short time experiment	0.24	6.5	97	3.1
Long time experiment	0.69	6.0	92	3.3

[a] c^* = concentration of lactic acid after 5- and 20-hour experiment.

The values of both η and η_{EC} confirm an effective conversion of lactate to lactic acid. Another positive effect is that sodium hydroxide, produced in the cathode compartment, can be used for the neutralization of a fermenting broth, thus enhancing the economy of the technique.

Long-time experiments reveal the effect of the phenomena coupled to electrotransport. The experiments and a detailed analysis of effects which depress the current efficiency and limit the final concentration of the acid will be the topic of our next paper.

CONCLUSIONS

- For the conversion of lactate to lactic acid in an electrodialysis unit, the effects of concentration polarization and, primarily, the low conductivity of LA, depress the current efficiency and enhance energy consumption.
- By filling the lactic acid compartment with a suspension of the cation-exchange resin in the hydrogen form, which also acts as the conducting turbulence promoter, it was possible to increase the limiting current density from 2.7 ± 0.3 mA/cm^2 (without the resin) to 18.3 ± 2 mA/cm^2 (with the resin). With such a current density the rate of lactic acid formation was 6.0 $mol \cdot m^{-2} \cdot h^{-1}$, the current efficiency was 92%, and energy consumption was 3.3 $kW \cdot h \cdot kg^{-1}$.
- It can be generally concluded that for electrodialysis units applied for the recovery of carboxylates from broths and the conversion of the salts to acids (lactic, acetic, propionic), a conducting turbulence promoter that increases conductivity in the weak acid compartments will enhance the productivity.

ACKNOWLEDGMENT

This work was supported by Copernicus Project ERB-CIPA-CT92-3018.

REFERENCES

1. B. Kharas, F. Sanchez-Riera, and D. K. Severson, "Polymers of Lactic Acid," in *Plastic from Microbes. Microbial Synthesis. Polymers and Polymer Precursors* (D. P. Mobley, Ed.), Hanser Publishers, Munich, 1994, p. 93.
2. F. F. Kuppinger, C. Busch, and C. Eigenberger, *DECHEMA Biotechnology Conferences 5*, VCH Verlagsgesellshaft, 1992, p. 671.
3. J. Johann, F. F. Kuppinger, and G. Eigenberger, in *Biochemical Engineering—Stuttgart* (M. Reuss, H. Chmiel, E. D. Gilles, H. J. Knackmuss, and G. Fischer, Eds.), Stuttgart, 1991, p. 274.
4. M. Harju and M. Heikonen, US Patent 4,855,056 (1989).
5. R. Datta, US Patent 4,885,247 (1989).

6. A. de Raucourt, D. Girard, Y. Prigent, and P. Boyaval, *Appl. Microbiol. Biotechnol.*, *30*, 521 (1989).
7. A. de Raucoust, D. Girard, Y. Pringent, and P. Boyaval, *Ibid.*, *30*, 528 (1989).
8. M. Czytko, K. Ishii, and K. Kawai, *Chem. Ing. Tech.*, *59*, 952 (1987).
9. G. Vlaemynck, P. Treast, and J. de Vilder, *Meeded. Fac. Landbouwwet Rijksuniv. Gent*, *54*, 1369 (1989).
10. V. V. Kotelev, G. A. Litynsky, M. K. Bologa, and A. K. Rudakov, *Electron. Obrab. Mater.*, *5*(143), 63 (1988).
11. D. Rehmann, M. Heyde, W. Holley, and W. Bauer, *Chem. Ing. Tech.*, *64*, 286 (1992).
12. V. Heriban, J. Škara, E. Štrudik, and J. Ilavsky, *Biotechnol. Tech.*, *7*, 63 (1993).
13. P. Boyaval, C. Corre, and S. Terre, *Biotechnol. Lett.*, 9, 207 (1987).
14. Y. Nomura, M. Iwahara, M. Hongo, *Biotechnol. Bioeng.*, *30*, 788 (1987).
15. V. Mavrow, W. Pusek, O. Kominek, and S. Wheelwright, *Desalination*, *91*, 225 (1993).
16. W. C. B. Mandersloot and R. E. Hicks, *Ind. Eng. Chem., Process. Des. Dev.*, *4*, 305 (1965).
17. Y. Tanaka, *J. Membr. Sci.*, *57*, 217 (1991).
18. S. J. Judd, C. S. Solt, and T. Wen, *J. Appl. Electrochem.*, *23*, 1117 (1993).
19. H. Mioyoshi and T. Fukomoto, *Sep. Sci. Technol.*, *23*, 585 (1988).
20. Y. Tanaka, M. Iwahashi, and M. Kogure, *J. Membr. Sci.*, *92*, 217 (1994).
21. K. Kontturi, S. Mafe, J. A. Manzanares, L. Murtomäki, and P. Viinikka, *Electrochim. Acta*, *39*, 883 (1994).
22. D. A. Cowan and J. H. Brown, *Ind. Eng. Chem.*, *51*, 1445 (1959).
23. O. Kedem and Y. Maoz, *Desalination*, *19*, 465 (1976).
24. W. R. Walters, D. W. Weiser, and L. J. Marek, *Ind. Eng. Chem.*, *47*, 61 (1955).
25. V. D. Stankovič, *J. Appl. Electrochem.*, *24*, 525 (1994).
26. J. M. Chiapello and M. Bernard, *J. Membr. Sci.*, *80*, 251 (1993).
27. C. E. Pike and C. H. Seager, *Phys. Rev. B.*, *10*(4), 1435 (1974).
28. R. Wódzki and A. Narębska, *J. Appl. Polym. Sci.*, *30*, 769 (1985).
29. F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, NY, 1962.

Received by editor February 25, 1997
Revision received July 1997