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Purification of organic acids using electrodialysis with bipolar membranes (EDBM) combined with monovalent anion selective membranes

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Abstract:

The feasibility of using electrodialysis with bipolar membranes (EDBM), combined with monovalent selective anion exchange membranes was investigated to purify organic acids from fermentation broths or wastewater streams. A simulated beet molasses feed containing a mixture of monobasic lactic acid and polybasic citric acid was used for this purpose. The impact of the feed pH, the configuration of the membrane stack and the voltage applied on the selectivity of the process was investigated. At a pH of 9~10 and an electric field intensity of 9 V/cm, a lactic acid product with a purity of at least 97% can be obtained by using both two chamber (BP-A) and three chamber (BP-A-C) configurations with the monovalent selective membrane. When using the BP-A configuration, the hydroxide ions generated by the bipolar membrane compete with the lactate anions to move into the acid solution and so the energy efficiency is lower than with the BP-A-C configuration. To mimic a multiple pass process and increase the lactic acid concentration of the final product, experiments were performed across a range of volume ratios between the feed and acid solutions. As this ratio is varied, the purity of lactic acid produced remains higher than 95% while the energy consumption is essentially unaffected. Due to the osmotic flow of water during experiments, the highest lactic acid concentration that can be achieved is limited to 153 g/L at a volume ratio (V_A: V_F) of 1:10.

Keywords: Monovalent ion exchange membrane, citrate, lactate, beet molasses

1. Introduction:

Organic acids such as lactic acid and citric acid are used widely in both the food and pharmaceutical industry as preservatives [1], chemical intermediates [2] or buffer media [3]. In addition, there is a growing demand for these compounds in the production of biodegradable plastics [4]. Organic acids are produced commercially either by fermentation or chemical synthesis. The former is preferred due to its lower cost and as many food quality laws stipulate that acids used in foods must be of biological origin [5]. In addition to fermentation processes designed specifically for organic acid production, the by-product or wastewaters of industrial processes such as ethanol production (stillage) [6], sugar-beet processing (beet molasses) [7], agricultural production and even human sewage [8] also contains numerous organic acids or organic acid salts. The recovery of those organic anions can not only reduce the environmental impact associated with their disposal, but also produce organic acid products of high economic value.

Membrane processes such as nanofiltration [9], diffusion dialysis (DD), conventional electrodialysis (ED) and electrodialysis with bipolar membranes processes (EDBM) are widely used in the recovery or production of such organic acids [5, 10-13], as they eliminate the waste or salts produced by other processes. However, a mixture of organic acids is often present. For example, the fermentation broth of succinic acid production contains lactate [14], acetate and formate [9] as by-products; the stillage of ethanol production contains glycerol, lactate and succinate [6]; beet molasses is known to contain a high concentration of lactic acid (2~5 wt%) and a somewhat lower one of citric acid (1~2.5wt%) [7, 15-19]. Traditional membrane technologies do not have a high selectivity between these different organic anions, so direct use of the organic acid recovered by these processes is not possible and further processing steps are required to increase the acid purity. Chromatography [14, 20-22], solvent extraction [23] and pressure driven filtration[9, 24] have been proposed for this purpose, but these methods have some disadvantages. Chromatography produces significant volumes of effluent [21, 25], solvent extraction requires the management of hazardous and often toxic solvents and the expense of solvent recovery, while fouling during filtration processes also needs to be addressed [26]. EDBM is a cost-effective and environmentally friendly approach, but it has low selectivity between ions of similar charge. To improve the selectivity of the traditional EDBM process, monovalent anion selective membranes can be used [27, 28]. To date, such membranes have mainly been explored for separation between mono and multi-valent inorganic anions, such as the rejection of carbonate and sulphate [29], defluorination [30] and the treatment of nitrate-containing effluents [31] and there are no reported studies on the separation of organic acid ions. In this study we seek to address this gap, with a study of the application of EDBM with monovalent selective membranes to the extraction of organic acids with high purity. A simulated beet molasses solution which contains a mixture of lactic acid ($C_3H_6O_3\%$) and citric acid ($C_6H_8O_7$) is used to evaluate the feasibility of this approach.

2. Experimental

2.1 Materials

The membranes used are the Neosepta ACS monovalent selective anion exchange membrane, AMX anion exchange membrane, CMB cation exchange membrane and BP-1E bipolar membrane, all supplied by Astom (Tokyo, Japan). The properties of these membranes are recorded in Table 1. Before the experiments, all membranes were immersed in 0.1 mol/L NaCl solution for 24 h and then washed in purified water (13.2 MΩ cm, Millipore) several times to ensure that they were in the Na^+ and Cl^- forms and all mobile ions have been removed.

Table 1. Properties of the membranes used in this study[a]

Properties	Unit	Membranes			
		ACS	AMX	CMB	BP-1E
Thickness	μm	130	140	210	220
Resistance[b]	$\Omega\cdot cm^2$	3.8	2.4	4.5	-
Water splitting voltage[c]	V	-	-	-	1.2
Water splitting efficiency	%	-	-	-	>98

[a]. Data obtained from the product brochure provided by manufacturers. [b]. Equilibrated with a 0.5 mol/L NaCl solution at 30 ℃. [c]. Measured with 1 mol/L NaOH and HCl at 100 mA/cm^2 at 30 ℃

Lactic acid (85%~90%), potassium phosphate monobasic (KH_2PO_4, 99.5%), phosphoric acid (H_3PO_4, 85%~90%) and sodium chloride (NaCl, 99.5%) were procured from Shanghai Macklin Biochemical Co., Ltd. Sodium hydroxide (NaOH, 97%), Sodium sulphate (Na_2SO_4, 99.9%) and citric acid monohydrate ($C_6H_8O_7\cdot H_2O$, 99.8%) were purchased from Shanghai Aladdin Biochemical Technology Co. Ltd. An analytical standard of lactic acid (90 wt%) for HPLC was purchased from Sigma-Aldrich. Purified water (13.2 MΩ cm, Millipore) was used for preparing all solutions used in this work.

2.2 EDBM set-up and operation

Two arrangements are studied within the integrated EDBM stack. In the BP-A configuration, there are two cell pairs, each containing a feed and an acid compartment (Figure 1 (a)). In the BP-A-C configuration, there are two cell triplets, each containing an alkali, a feed and an acid compartment (Figure 1 (b)). Each compartment is regulated by specially designed millimetre-thick silica gel spacers with a thickness of 0.75 mm. The electrodes are made of titanium coated with ruthenium. The membranes and electrodes have the same effective area (189 cm^2, 9 cm width and 21 cm length).

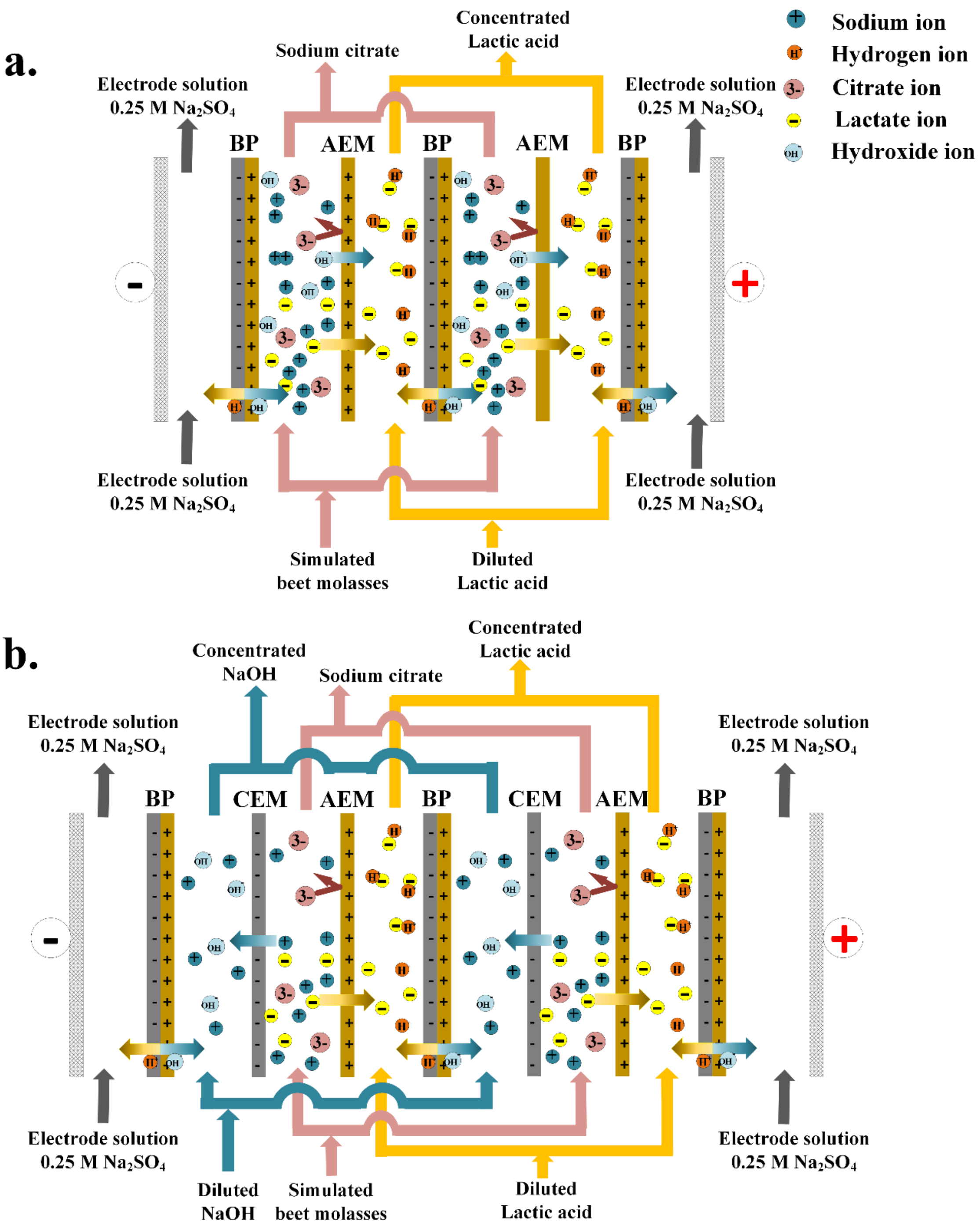

Figure 1. EDBM set-up with (a) BP-A configuration and (b) BP-A-C configuration. BP= bipolar membrane, CEM= cation exchange membrane, AEM = anion exchange membrane.

When changing the configuration of the membrane stack from BP-A-C to BP-A, the distance between the two electrodes is reduced from 1 cm to 0.8 cm, as there are fewer membranes. For consistency, the applied voltage was thus reduced to maintain the same field intensity in V/cm, where this is equal to the applied potential (V) divided by the distance between these two electrodes in cm. The experiments were operated under such constant field intensity in V/cm with a regulated power supply (IT633A, Itech Electronic Company Ltd). Operating in this mode is preferred in batch operation because it can reduce the possibility of the system operating beyond the limiting current density.

Unless otherwise noted, 300 mL of simulated beet molasses was prepared as the feed solution by adding 2 wt% (0.22M) of lactic acid and 2 wt% (0.10M) of citric acid) and then adjusting the pH (3.7 ± 0.1, 5.5 ± 0.1 or 9~10) using NaOH. The initial solution of acid was 0.009 M lactic acid, that of the alkali 0.01 M NaOH and electrolyte 0.25 M Na_2SO_4, respectively. Each chamber was connected to a corresponding beaker, with each solution circulated by a peristaltic pump (BT100-2J, Longer Precision Pump Co., Ltd) with a flow rate of 300 mL/min.

The pH of the feed solution was adjusted by regular additions of sodium hydroxide (1.9 M) when needed to maintain the initial value throughout the experimental period.

2.3 Analysis

Determination of lactate and citrate concentrations was carried out according to the methods reported in the literature [7, 32] using a high-performance liquid chromatography (HPLC, Shimadzu) system with a UV–Vis detector at a wavelength of 190 nm and 210 nm. An InertSustain^{TM} AQ-C18 column (4.6×150 mm) (Shimadzu) was used with a mobile phase of 10 mM KH_2PO_4 solution at a pH of 2.9 at 1 ml/min and 40 °C.

The concentration of alkali generated in the base chamber was determined by titration with sulphuric acid solution (0.01 mol/L).

The lactate purity(%La) in the acid solution is defined as its mol fraction of the two organic anions present as shown in Equation 1.:

$$\%\mathrm{La}=\frac{C_{La,t}^{A}\times V_t^A}{C_{La,t}^{A}\times V_t^A+C_{C,t}^{A}\times V_t^A}\times 100\% \qquad (1)$$

where $C_{La,t}^{A}$ and $C_{C,t}^{A}$ refer to the lactate and citrate concentration in the acid solution after being treated for t mins, respectively. V_t^A is the volume of the acid solution after being treated for t mins.

The current efficiency ($\%\eta$, Equation 2) was calculated based on the initial (t=0) and final concentrations of lactate in this acid chamber.

$$\%\eta=\frac{z\cdot(C_{La,t}^{A}\times V_t^A-C_{La,0}^{A}\times V_0^A)\cdot F}{N\cdot I\cdot t}\times 100\% \qquad (2)$$

where F is the Faraday constant (96,500 C); N is the number of repeat cells (two); I (A) is the current applied in the stack and t (s) is the total test time; z is the valence of organic ion; V_0^A is the initial volume of acid chamber.

The energy consumption per kg of lactic acid produced, E (kWh/kg HLa) was calculated from Equation 3:

$$E = \int_0^t \frac{U \cdot I \cdot dt}{(C_{La,t}^{A} \times V_t^{A} - C_{La,0}^{A} \times V_0^{A}) \cdot M} \quad (3)$$

where U (V) is the voltage drop across the EDBM stack and M is the molar mass of the acid (90.08 g/mol).

Unless otherwise stated, all experiments were repeated twice to determine the error, which is represented as two standard deviations either side of the mean. For specific experiments, the percentage error of earlier experiments was used to provide the error bars needed to assess whether data was significantly different.

3. Results and discussion

3.1 Selectivity optimization of the EDBM process

The permselectivity of an ion exchange membrane (IEM) is governed by several factors, such as the hydrated radii of the ions, their affinities with the IEM and their migration rates (diffusivity) in the membrane phase. The monovalent membrane used in this study (Neosepta ACS) is prepared by a “paste method” with a highly cross-linked layer deposited on its surface [29, 33, 34]. By introducing such a dense skin layer , the membrane selectivity for ions with different hydrated radii increases due to a size sieving effect [35]. As a commercial membrane, the details of the Neosepta ACS structure and preparation method are confidential, so it is unclear whether there are other factors that work to further improve this selectivity.

The pH value of beet molasses ranges from 3 to 6 [7, 36, 37]. The simulated solution prepared from 2 wt% citric and 2 wt% lactic acid had a pH of 3.7. Under these conditions, about 74% of the citrate present is dissociated and predominantly exists as the monovalent ion $C_6H_7O_7^-$ (Figure S1). Conversely, only about 40% of the lactic acid is dissociated, again forming a monovalent anion. Table 2 shows that there is a big difference between the Stokes radii of these two species, indicating that a permselective anion-exchange membrane which has a size sieving capacity should be effective. Indeed, Figure 2 (a) shows that the use of the permselective (ACS) anion-exchange membrane within a BP-A-C configuration provides a much greater purity of lactic acid when a simulated beet molasses with a pH value of 3.7 is introduced than a more standard (AMX) ion exchange material. Citrate and lactate anions are transferred from the feed chamber to the acid chamber in a molar ratio of 1:1 for the AMX membrane and 1:9 for the ACS membrane when deployed at 6 V/cm. However, due to the dense skin layer, the rate of transport of ions is lower when the ACS membrane is used, as indicated by the current density falling from around 5.5 mA/cm^2 with the AMX to around 3.2 mA/cm^2 with the ACS (see Figure 2(c)).

The same EDBM stack was readily deployed at 12V/cm with the ACS membrane (Figure 2 (d)). However, it was not possible to initially achieve such a high voltage with the AMX membrane, due to its lower resistance and subsequent high current density. After 30 minutes, the voltage could be adjusted to 12 V/cm, as the solution resistance had increased due to the transfer of ions from the feed into the acid solution. After 45 minutes, the lactate purity increased from 50% to 70% (Figure 2 (b)). This was due however, to the depletion of citrate in the feed chamber during this period rather than any change in the membrane performance, as is evident from the rapidly falling current shown in Figure 2(d).

Table 2 The stokes radius of organic acid ions in this study

Species	Stokes radius (nm)
Lactate ion $(C_3H_6O_3{}^-)$ [38]	0.23[a]
Dihydrogen citrate ion $C_6H_7O_7^-$ [39]	0.303[b]
Citrate ion $C_6H_5O_7^{3-}$ [40]	0.394[b]

[a.] *data is obtained directly from the literature; b. data is calculated based on the diffusion coefficient of ions through the Stokes-Einstein relationship[41] (* $r^s = \frac{KT}{6\pi\eta D_i}$ *).*

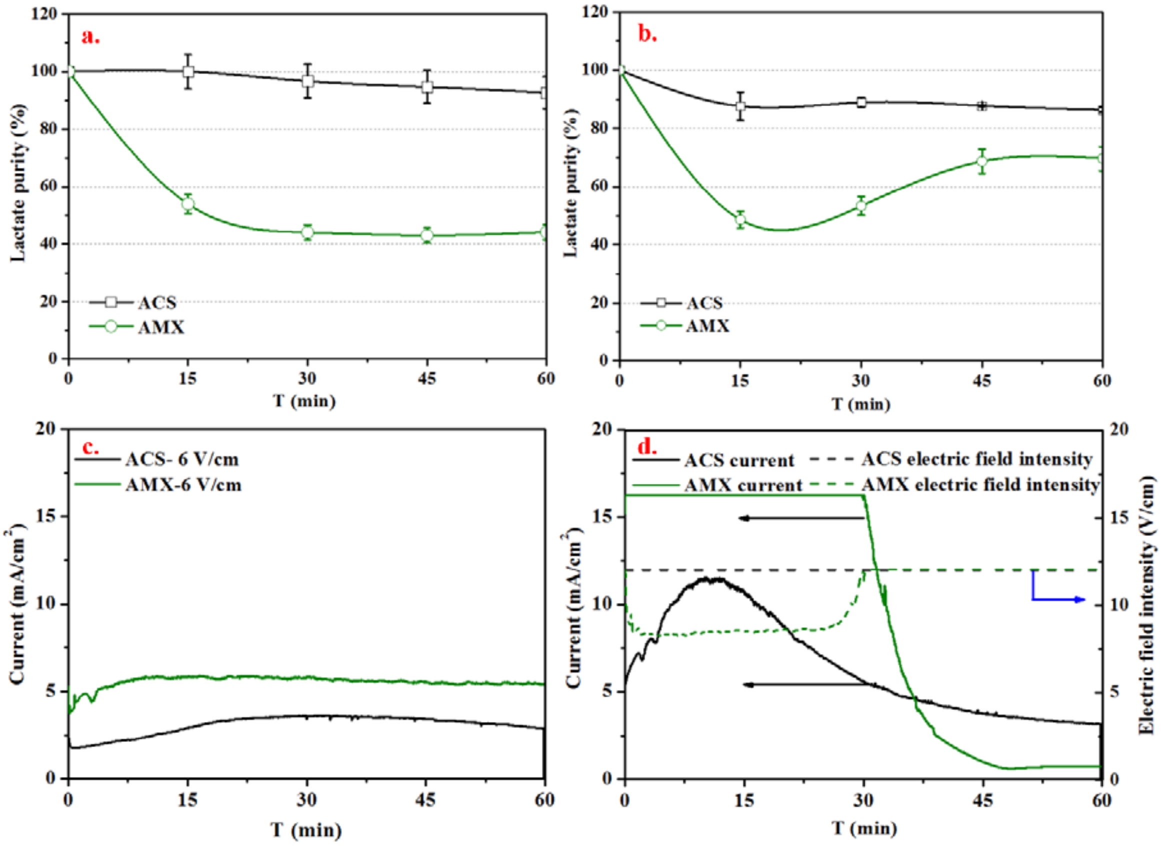

Figure 2 The lactate purity(%La) in the acid solution (a) and the current density of the ED unit (c) when the electric field intensity is 6 V/cm; the lactate purity(%La) in the acid solution (b) and the current density & electric field intensity of the ED unit (d) when the electric field intensity is 8-12 V/cm. (pH of feed solution: 3.7, BP-A-C configuration)

At a high pH, polybasic acids such as citrate present as ions with a higher valence (see Figure S1). These species have a greater number of water molecules in their hydration shell [42], which then leads to a larger hydrated or Stokes radius (Table 2) [43]. The stronger attraction for H_2O molecules to these multivalent species also means that they are less prone to dehydration, as can occur at the water membrane interface [44] due to the drag forces induced by the voltage gradient. To determine the impact of these effects, experiments were conducted at variable pH with the ACS membrane, by adjustment with sodium hydroxide. When the pH value is less than 4, most of the citrate ions are present in a monovalent form; when the pH value is ~5.5 they are mainly divalent and if the pH value increases beyond 9, almost all are trivalent (Figure S1). As shown in Figure 3 (b), when the pH value of the feed solution is greater than 9, the purity of the lactic acid in the acid chamber approaches 93%, due to the slower migration of the large, fully hydrated trivalent citrate species. At the same time, a higher pH value corresponds to a higher current density (Figure S2 (b)) and greater transfer rate of lactate (Figure 3 (a)), as with a higher pH value, more lactic acid dissociates, increasing the concentration driving force for this species to migrate and improving the conductivity of the feed solution. Thus, from the perspective of both the feed solution processing rate and the purity of the lactic acid product, adding NaOH to the feed solution to increase its pH value is a good approach. Of course, the financial cost of this addition and the required pH of the final product will also determine whether such an approach is viable.

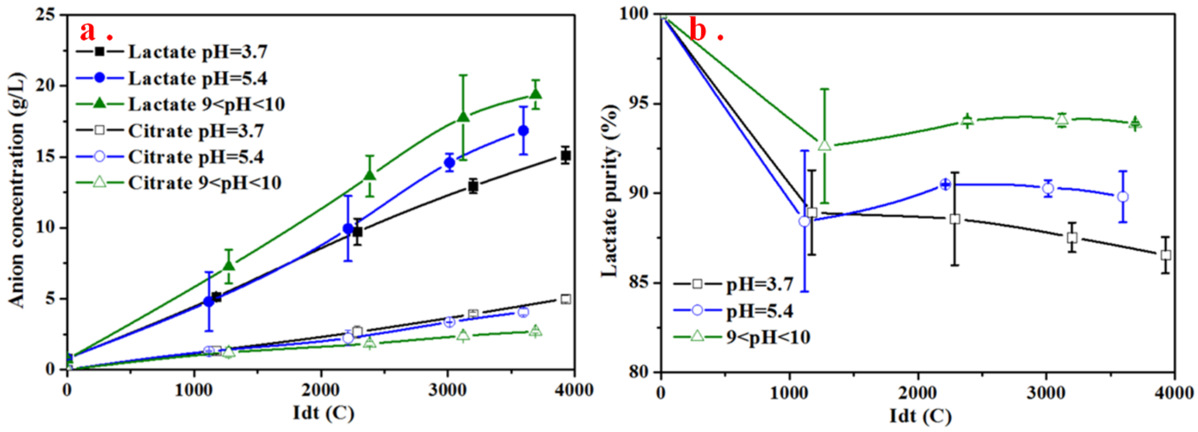

Figure 3 The effect of feed solution pH a. the concentration of lactate and citrate in the acid chamber (g/L) and b. the lactate purity versus total charge (C) transferred. (12 V/cm, BP-A-C configuration with an ACS anion exchange membrane)

Other workers have shown that the depletion of monovalent ions from the boundary layer of a monovalent selective membrane at a high current density[45] can lead to increased transport of the multivalent ions and thus lower ion selectivity [45-48]. As shown in Figure 4, the amount of citrate ions transferred to acid chamber is higher at 12 V/cm than at lower voltages due to a similar increase in current density (see Figure S3) and thus boundary layer depletion. Operation at lower voltages leads to an increase in the purity of lactic acid obtained in the acid chamber from 93 to 97%, consistent with the trend shown for inorganic ion solutions [45-48].

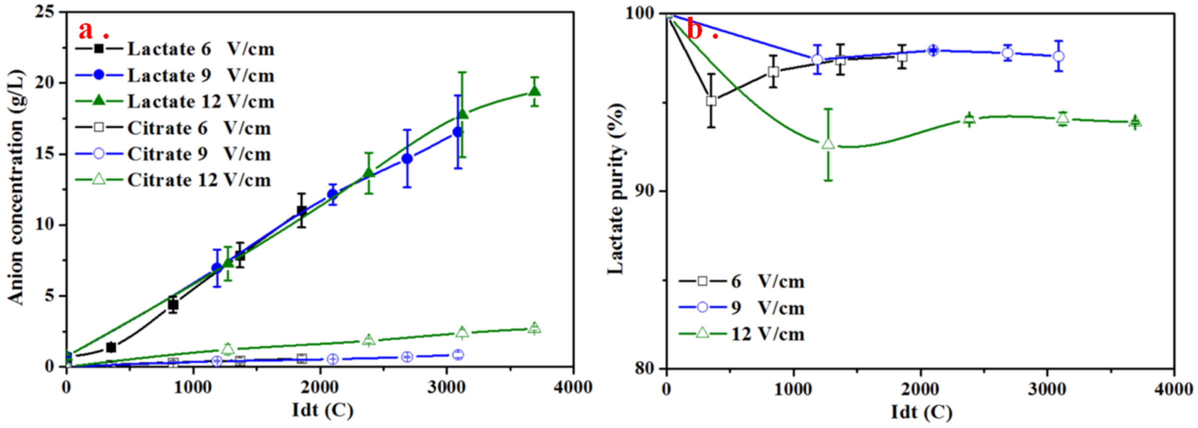

Figure 4 The effect of applied electric field intensity, a. the concentration of lactate and citrate in the acid chamber and b. the purity of lactic acid in acid chamber versus total charge (C) transferred. (pH of feed solution: 9~10, BP-A-C configuration)

The energy consumption (kWh per kg of lactate transferred to acid chamber) is higher at 12 V/cm than at 9 or 6 V/cm (Figure 5). This can partly be explained by the increase of citrate ion transfer at 12 V/cm, but may also reflect higher levels of water splitting at the ion exchange membranes as the voltage is increased. While water splitting at the bipolar membranes is desirable, when it occurs at the cation and anion exchange membranes it serves mainly to alter the pH of the feed solution and thus wastes energy. The energy consumption of lactic acid production when achieving 80% of lactate transfer is similar to the value when achieve 50% of lactate transfer, indicates that the back diffusion of lactate ions is not a dominant factor for energy consumption when dealing with a feed solution that contains 20 g/L of lactate and at a volume ratio of 1:1 (feed solution to acid solution).

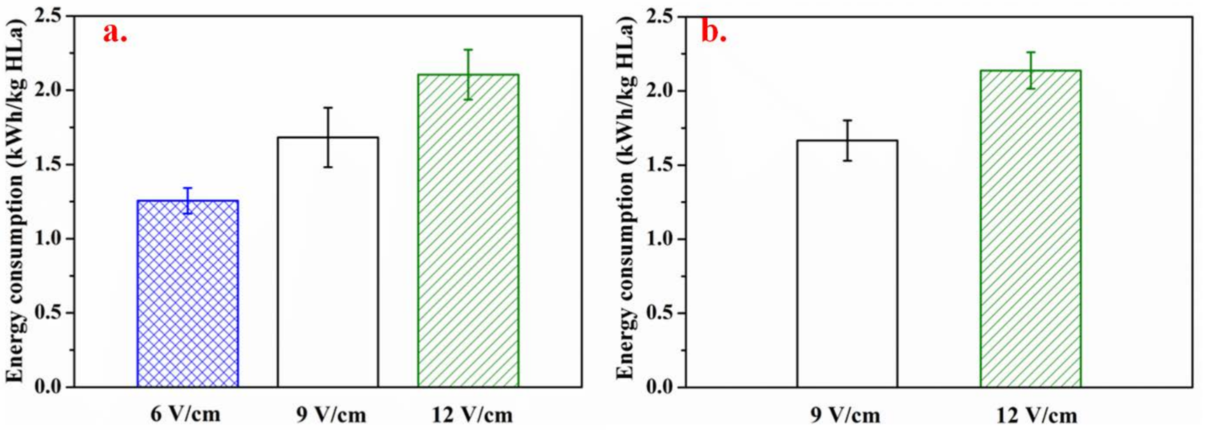

Figure 5 Energy consumption of the EDBM process as a function of electric field intensity when achieving a a. 50% and b. 80% transfer of the lactate from the feed solution

(pH of feed solution: 9~10, BP-A-C configuration)

3.2 Configuration of EDBM membrane stack

With the BP-A-C configuration, the pH value of the feed solution decreases with time due to the transfer of hydroxide ions into the acid chamber. To maintain the pH, a regular addition of NaOH solution is necessary. As shown in Table 3, the NaOH generated in the base solution is more than the amount of NaOH consumed in maintaining the pH. Using a BP-A configuration, which combines the feed and base chambers has the potential to simplify the process and at the same time, maintain the pH value of the feed solution above 9.

Table 3 NaOH consumed/generated in feed/base solution (configuration: BP-A-C, pH of feed solution: 9~10)

Voltage (V/cm)	lactate transfer from the feed solution	Processing time (min)	NaOH consumed in feed solution (mol)	NaOH generated in base solution (mol)
6	50 ± 2%	60 ± 5	0.014 ± 0.002	0.044 ± 0.002
9	50 ± 2%	30 ± 5	0.007 ± 0.001	0.032 ± 0.001
12	50 ± 2%	15 ± 5	0.007 ± 0.001	0.035 ± 0.004
9	80 ± 2%	45 ± 5	0.013 ± 0.001	0.055 ± 0.004
12	80 ± 2%	30 ± 5	0.012 ± 0.001	0.063 ± 0.004

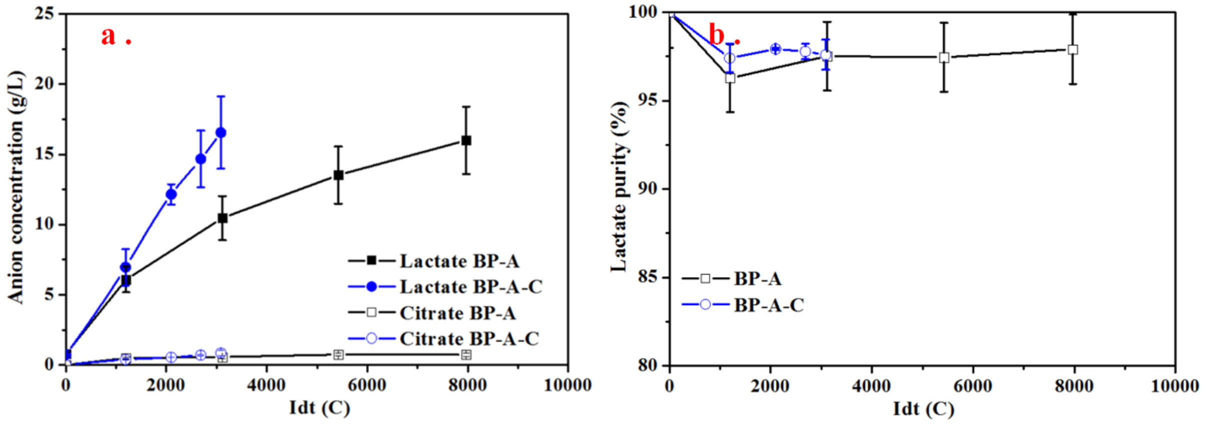

Figure 6 a. the concentration of lactate and citrate in acid chamber and b. the purity of lactate in acid chamber versus total charge (C) transferred for two different cell configurations. (pH of initial feed solution: 9~10, voltage: 9 V/cm)

At an electric field intensity of 9 V/cm, there is no significant difference in lactic acid purity (Figure 6 (b)) when using the different configurations. However, with the BP-A-C configuration, NaOH addition was used to keep the pH of feed solution in the range of 9 to 10; conversely, for the experiment with the BP-A configuration, the OH^- generated by the bipolar membrane was transferred to the feed solution directly. This caused the pH value in this chamber to increase from 9.14 to 11.20 in 5 mins and further to 12.07 after 60 mins. When the pH increases to these values, the transport of OH^- competes with that of lactate more effectively. This causes the reduced rate of lactate transfer shown in Figure 6(a). Further, the hydroxide transfer significantly increases the energy demand of the EDBM system, as shown in Figure 7.

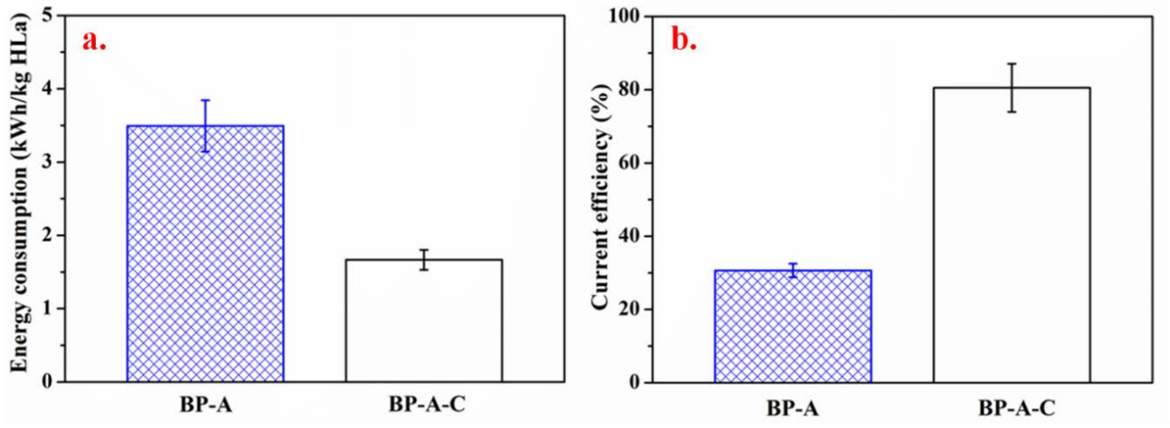

Figure 7 a. Energy consumption and b. current efficiency of BMED process when using different configurations (at 80 ± 2 % of lactate transfer from the feed solution, pH of initial feed solution: 9~10, voltage: 9 V/cm)

When using a BP-A-C configuration, the H^+ and OH^- generated by the bipolar membrane transfers to the acid and base chamber respectively and the pH of the feed solution is maintained at 9~10 by adding additional NaOH solution. When using a BP-A configuration, the H^+ and OH^- generated by the bipolar membrane transfer to the acid and feed chamber respectively; causing the pH value of the feed to rapidly increase. This transfer of OH^- consumes energy, leading to a higher energy consumption for this configuration (Figure 7) and lower current efficiency (31% vs 74%). Further, it is hard to control this pH, especially over longer processing times.

3.3 Volume ratio between feed and acid solution

In the experiments described above, the volumes of the solutions in acid, base and feed chambers are all 300 mL. In this case, the highest lactic acid concentration that can be obtained is equal to the lactate concentration in the feed solution (20.0 ± 2.0 g/L). To reduce capital costs and increase the final acid concentration, a multistage-batch or feed and bleed operation may be used in industry [50]. At the lab scale, a multistage-batch situation can be modelled by changing the volume ratio of diluate (feed) to concentrate (acid) solution.

The experiments in this section were performed at 9 V/cm with feed solutions of 27.5 ± 2.5 g/L of lactate and 20 ± 2.0 g/L of citrate (pH 9~10). The volumes of acid and base solutions were maintained at 300 mL, while the volume of the feed solution was increased from 300 mL, to 1500 and to 3000 mL. As shown in Figure 8, the rate of increase in lactic acid concentration in the acid chamber is essentially unaffected by the feed volume in the early stage of each experiment, as the composition of the solutions on both sides of the membrane are similar. However, the highest lactic acid concentration that can be achieved increases with the volume ratio while the purity of the lactic acid in acid chamber is maintained above 95% (Table 5). As the experiment continues, the rate of increase in lactic acid concentration slows due to the osmotic flow of water. The lactic acid concentrations stabilise when around 20000 (for 1 to 5) or 35000 Coulombs were consumed (for 1 to 10), even though the feed solution still contains lactate ions (2.5 ± 1.3 g/L for 1:5 case and 8.3 ± 1.3 g/L for 1:10 case). At this point, the water transfer caused by osmosis and electro-osmosis (the latter being dominant [51, 52]) will dilute the acid solution and the number of lactate ions transferred from the acid chamber to the feed chamber by diffusion balances that transferred from the feed to the acid chamber by the electric field. For example, when $V_F:V_A=10$, the final concentration of lactic acid in acid solution is 153 g/L, which is less than the theoretical maximum of 10 times the initial feed lactate concentration (27.5 g/L). Thus, while increasing the volume ratio can produce a lactic acid product of higher concentration, there remains a limit due to the water transfer and the back diffusion of lactate ions.

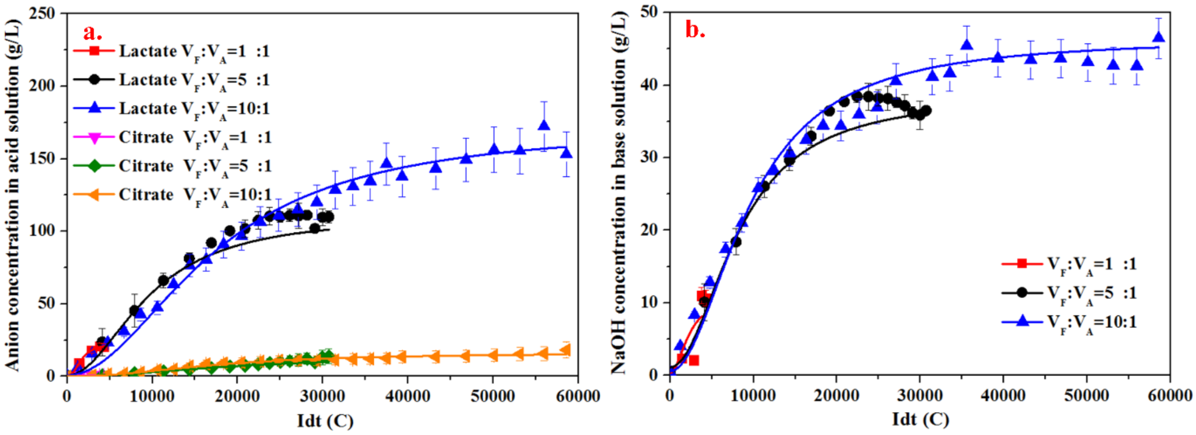

Figure 8 a. The concentration of lactic acid and citric acid in the acid chamber and b. the concentration of NaOH in the base chamber versus total charge (C) transferred when changing the volume ratio of feed solution and acid solution.(pH of initial feed solution: 9~10, voltage: 9 V/cm, BP-A-C configuration)

The trends in NaOH concentration in the base chamber are similar to that of the lactate concentration in the acid chamber (Figure 8b). At the end of experiments, the final NaOH concentration in the base solution when using a volume ratio of 1:10 is 1.16 mol/L (46.5 g/L, Table 5), which is much lower than the concentration of lactate (~1.70 mol/L) in the corresponding acid solution. This can be explained by the greater water transfer and back diffusion for the NaOH system. As shown in Table 5, the volume change in the base solution is larger than that of the acid solution, indicating that there is a greater osmotic flow of water into this chamber. During these experiments, the pH of the acid solution remains below 3. Thus, as the lactate ions move into the acid chamber, most of them will combine with the hydrogen ions generated by the bipolar membrane and form neutral lactic acid molecules. This reduces the total osmotic pressure and thus the osmotic flow of water. Further, these uncharged molecules cannot cross through the ion-exchange membranes, so the back diffusion of lactic acid is also reduced.

Table 5 Concentrations, volumes and purities achieved in the acid and base chambers for different acid: feed volumes. (at 82 ± 2% of lactate transfer from the feed solution; initial feed solution: pH 9~10, 27.5 g/L lactic acid, 20 g/L citric acid. voltage: 9 V/cm, BP-A-C configuration)

Chamber	V_A: V_F	1:1	1:5	1:10
Acid solution	Lactic acid purity (%)	98.0 ± 0.3^{a}	96.9 ± 0.8	95.1 ± 1.9^{a}
	Lactic Acid Concentration (g/L)	21 ± 2	100 ± 3	153 ± 10
	Volume (mL)	305 ± 10^{b}	342 ± 3	370 ± 10^{b}
Feed solution	mol fraction of Citrate ion^{a} (%)	68.3 ± 0.6	66.0± 1.0	59.5± 1.0
	Citrate ion Concentration (g/L)	20 ± 1	20 ± 1	18 ± 1
	Volume (mL)	289 ± 10^{b}	1394± 22	2579 ± 10^{b}
Base solution	Sodium Hydroxide Concentration (g/L)	11.0± 1.1	36.4± 0.1	46.5± 2.8
	Volume (mL)	309 ± 10^{b}	355 ± 3	564 ± 10^{b}

Note: a. the percentage error of former experiments was used. b. errors are based on the stated accuracy of the graduated cylinder.

As aforementioned, there is a limit to the lactic acid concentration that can be achieved for experiments with various volume ratios and processing time. For experiments with volume ratios of 1 to 5 and 1 to 10, this limit is reached within 240 mins and 780 mins (Figure 8), respectively. In the latter stages of these experiments, water transfer and back diffusion not only limits the final concentration but also increases the energy consumption of lactic acid production. This would suggest that the energy consumption should be higher for the cases with 1:5 and 1:10 volume ratio. A higher energy demand is certainly observed for the 1:10 volume ratio (Figure 9) but the energy demand for the 1:1 and 1:5 volume ratios are not significantly different. This may be because the solution resistance in the acid and base chambers falls as these concentrations increase balancing the other effects.

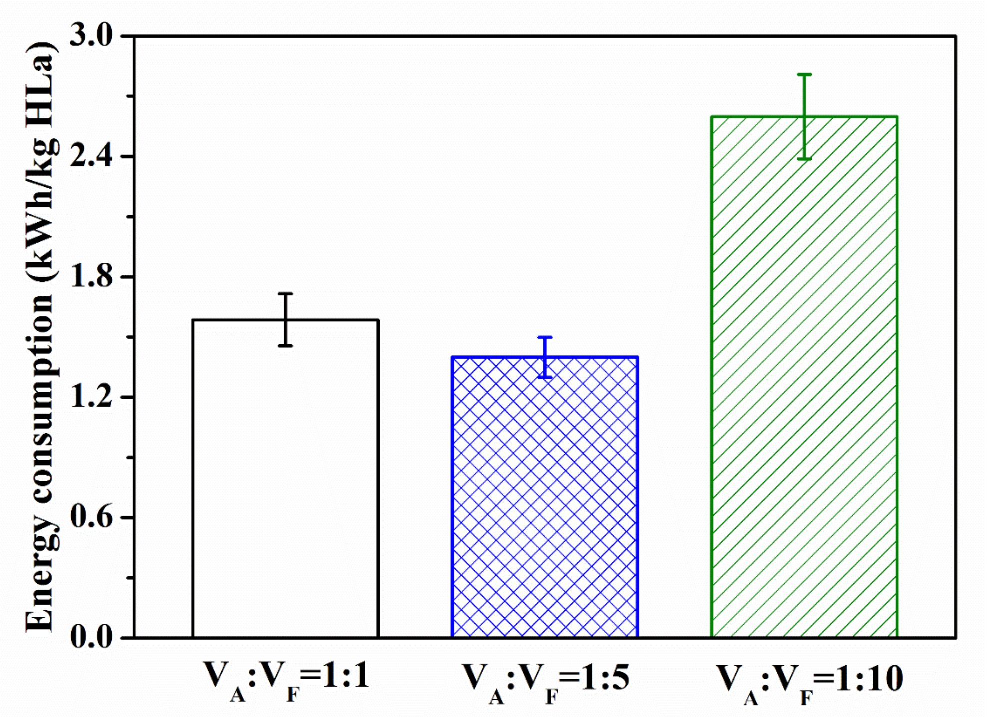

Figure 9 Energy consumption of HLa recovery when changing the volume ratio of feed solution and acid solution (at 82 ± 2% of lactate transfer from the feed solution; pH of initial feed solution: 9~10, voltage: 9 V/cm, BP-A-C configuration)

4. Conclusion

In this study, a simulated beet molasses solution was used to investigate the feasibility of using EDBM to recover lactic acid, a monobasic organic acid from a mixture with citric acid, a polybasic organic acid. Unlike inorganic acids, the dissociation of both mono-organic acids and polybasic organic acids can be affected by the pH of the aqueous solution. A higher pH value corresponds to a greater extent of dissociation of the organic acid and a higher valence of polybasic organic ions, which normally corresponds to a larger hydrated radius. In turn, this contributes to a higher selectivity. In this case, a pH value of 9~10, led to a lactic acid product with the highest purity (> 90%), as more than 99% of the citric acid was dissociated as the trivalent ion.

Compared with a BP-A-C configuration, a BP-A configuration could make full use of the hydroxide ions generated by the bipolar membrane to maintain the pH value of the feed solution. However, the superabundant hydroxide ions in the feed solution competed with lactate anions for transfer to the acid chamber, thus consuming energy. Although either configuration could produce a lactic acid product with a purity higher than 95%, the BP-A-C configuration was more energy efficient.

To mimic a multistage-batch situation and produce a more concentrated lactic acid product, experiments were also performed with various volume ratios of feed solution to acid solution. The volume ratio has little effect on the purity of final lactic acid product, so increasing the volume ratio is able to produce a lactic acid product with high purity and high concentration. Both the solution resistance of the acid and base chambers and the back diffusion of lactate ions affect the energy consumption of lactic acid production. In this study, there was no significant difference in energy consumption when the volume ratio was increased from 1:1 to 1:5 while it became much higher when the volume ratio was 1:10. Due to the osmotic flow of water during the process however, the highest lactic acid concentration that could be achieved was limited, so a combination with other methods would be needed if a higher concentration is needed.

Finally, it should be noted that this study was conducted with simulated solutions where membrane fouling is not anticipated. In a true industrial process, fouling may be caused by impurities within the feed solution including proteins and polysaccharides[53]. During ED, such membrane fouling can be controlled by adjusting flow conditions or solution pH [54] or changing cell configurations [55, 56]. Other methods, such as using pulsed electrical field [56], electrodialysis with reversed polarity, or operating in the overlimiting current density region have also been proposed [57]. Such membrane fouling needs a systematic study that is outside the scope of the present work.

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