# Citric acid production by electrodialysis with bipolar membranes

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## Abstract

Production of citric acid from sodium citrate was carried out by electrodialysis (ED), using bipolar membranes (BP) prepared from poly(phenylene oxide) (PPO). The process feasibility was tested using a laboratory ED-cell with an effective area 20 cm². Based on the configuration of BP-cation membranes (C)-BP, the performances of various sodium sulfate concentrations and sodium citrate concentrations are compared and discussed in terms of ionic transport and ion exchange. It is suggested that, in such an operation, the optimum concentration range be 0.5–1.0 M for sodium citrate and 0.25–1.5 M for sodium sulfate from the viewpoint of energy consumption, current efficiency and acid concentration. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Bipolar membrane; Citric acid; Electrodialysis; Water dissociation; Current efficiency

## 1. Introduction

Citric acid ($H_3Cit$) is of paramount industrial importance because, it is a useful product, which has been widely used in dairy, medicine and biochemical industries. The process currently used for the production of $H_3Cit$, is based on fermentation route [1]. As shown in Fig. 1, the raw materials such as maize, starch, grains, etc., are fermented and filtered. The filtered liquor is precipitated with lime followed by acidification with $H_2SO_4$, yielding citric acid and at the same time yielding large amounts of solid wastes such as $CaSO_4$. According to conventional procedure in China, 3–4 tons solid wastes will be formed for 1 ton products [1]. These large amounts of wastes give rise to serious contamination to the environment. Moreover, the product obtained by this technique is usually at low concentration, e.g. 0.2–1 N due to the limitation of fermentation process. Since, the fermentation process typically operates at near neutral pH; this being maintained via addition of a suitable base. Increasing the product concentration significantly reduces the productivity of the fermentor due to product inhibition.

Water splitting by bipolar membrane-electrodialysis (BPED) provides an attractive complement to the fermentation technology by removing the product acid, while simultaneously providing an equivalent amount of base for use in adjusting the pH in the fermentor as shown in Fig. 2. Compared with the conventional processes, several advantages are notable.

1. The new process does not needs any lime and thus produces no $CaSO_4$ solid wastes and the route is well simplified (precipitation, acidification and the followed filtration are cancelled).
2. The fermentor itself can now be operated at relatively low product concentration to assure high productivity.
3. The base is conserved in the system and no additional base is used to adjust the pH in the fermentor.
4. As an added advantage, the produced acid is usually at a relatively high concentration so that, the subsequent purification via crystallization or other techniques is relatively inexpensive.

Several studies have shown that this ED process, involving bipolar membranes (BP), have economic potential for recovering/producing organic/amino acids [2–6] such as lactic acid [7], acetate acid [8] as well as electroacidification of soybean protein [9,10].

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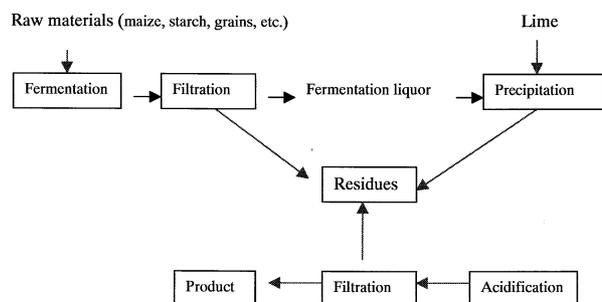Raw materials (maize, starch, grains, etc.)  Lime

Fig. 1. Schematic drawing of a conventional process for producing citric acid.

The principle of the electrodialytic water-dissociation process employing a BP is well documented. If a direct electrical potential (DC) is established between a BP, which consists of a layer of an anion exchange membrane and a layer of a cation exchange membrane, water dissociation occurs at the interphase and a current is sustained through the membrane by the migration of hydrogen and hydroxyl ions to the respective compartments under the fluency of applied DC electric field. By appropriately arranging conventional cation-exchange and anion-exchange membrane on either side of the BP, cations and anions of a given organic salt, e.g. sodium citrate ($Na_3Cit$) as discussed here, could be so directed to meet the $OH^-$ and $H^+$ in respective compartments to generate separate streams of alkali and citric acid.

Therefore, the aim of this work is to investigate an alternative process for the production of citric acid, which avoids the large amount of waste solution and the waste precipitation. We try to describe the results of experiments to obtain citric acid from different concentrations of support electrolyte (sodium sulfate) and organic salt (sodium citrate) employing BP.

## 2. Experimental

### 2.1. Material

Sodium citrate dihydrate of analytical grade was commercially obtained and used without further purification. The cation exchange membrane was prepared by sulphonating poly(phenylene oxide) (PPO) [11], the
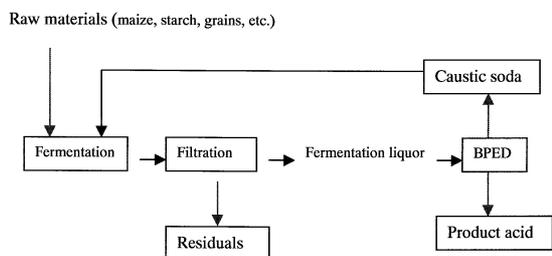
Raw materials (maize, starch, grains, etc.)

Fig. 2. Schematic drawing of a BPED process for producing citric acid.

Table 1
Main characteristics of the membranes

| Cationic membrane | Interpolymer type, sulfonic group |
| --- | --- |
| Area resistance ($\Omega$ cm$^2$) | <2 |
| Water content (%) | 30–40 |
| Transport number | >97% |
| Thickness (mm) | 0.18 |
| Ion exchange capacity (mmol dg$^{-1}$) | 1.6–1.9 |
| Anionic membrane | Interpolymer type, quarternary ammonium group |
| Area resistance ($\Omega$ cm$^2$) | <3 |
| Water content | 30–35 |
| Transport number | >98% |
| Thickness (mm) | 0.2 |
| Ion exchange capacity (mmol dg$^{-1}$) | 1.8–2.1 |
| Bipolar membrane | Composition of the cationic and anionic membranes |
| Area resistance ($\Omega$ cm$^2$) | <8 |
| Thickness (mm) | 0.3–0.5 |
| Potential drop in 1 M NaCl (V) | 1.5–3.0 (at 100 mA cm$^{-2}$) |

anion exchange membrane is prepared by brominating and quarter-aminating PPO [12] and the BP is obtained by casting the cation layer solution onto the anion layer [13]. Both the mono-polar membrane and BP were commercially obtained from Institute of Ocean Chemical Engineering of Shandong (China). The main characteristics were listed in Table 1.

### 2.2. Methods

The laboratory-scale experimental set-up was composed of one anode and one cathode as well as one piece of cation exchange membrane and two pieces of bipolar exchange membranes inserted between them to form four compartments, cathode compartment; acid compartment; salt compartment and anode compartment as shown in Fig. 3. The sodium citrate solution is fed to the acid compartment and support electrolyte solution, sodium sulfate solution, fed to the other compartments, if not specifically mentioned. Each compartment was connected to a separate external 1000 ml beaker, allowing for continuous recirculation (500 ml) by four centrifuge pumps (Model-D9463-125, Tuthill pump Co. of California, USA). The organic salt is converted into organic acid with the protons produced from the water dissociation transporting into the compartment and the sodium ions out of the compartment. The effective area of the membrane is approximately 20 cm$^2$.
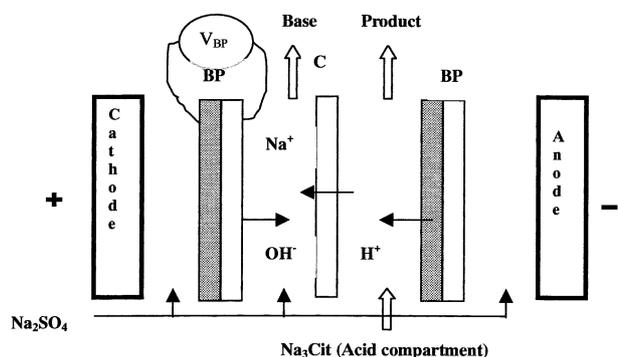
Fig. 3. Scheme of the laboratory water splitting cell for citric acid production. C, cation exchange membrane; BP, bipolar membrane. The name of compartment from the left is cathode compartment, base compartment, acid compartment and anode compartment, respectively.

The anode/cathode voltage difference was supplied by a CV/CC regulated power supply (YJ63, Shanghai Huguang Instruments works). The voltage drop across the stack was directly read from the indicators on the power supply, while the potential drop across a BP was measured with a Digital multimeter (model, GDM-8145, Good will instrument Co. Ltd., Taiwan) through two platinum probes near to the two surfaces of the layers. The concentration of citric acid was determined by titration with standard sodium hydroxide solution using phenolphthalein as indicator.

## 3. Results and discussion

### 3.1. Current–voltage curves

The current–voltage curves were measured under different concentrations of sodium citrate in the acid compartment and $Na_2SO_4$ in the other compartments. The results are depicted in Fig. 4. Obviously, the experimental $I-V$ curves for the three configurations show the typical behavior given by the coupling of ion transport and electrical field-enhanced water dissociation [14], at small voltage, the current is carried mainly by
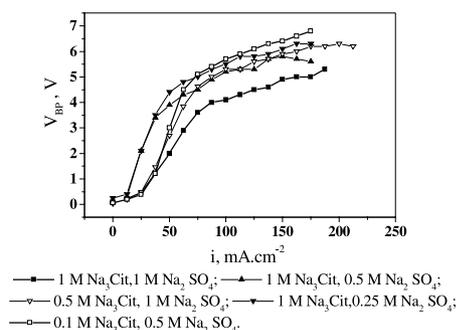


Fig. 4. Experimental $I-V$ curves at different concentrations, acid compartment containing citric sodium and others containing $Na_2SO_4$.

the salt ions and attains a limiting value. The resistance of the membrane increases more or less due to the migration of salt ions out of the bipolar junction; at high voltage, most of the current is carried by the $H^+$ and $OH^-$ ions generated by water dissociation taking place at the bipolar junction, and increases rapidly with the voltage. The membrane resistance then begins to decrease again with the applied voltage. The magnitudes of voltage values across a BP for the considered cases seems to follow the order that case 1 (1 M $Na_3Cit$, 1 M $Na_2SO_4$) < case 2 (1 M $Na_3Cit$, 0.5 M $Na_2SO_4$) ≈ case 3 (0.5 M $Na_3Cit$, 0.5 M $Na_2SO_4$) < case 4 (1 M $Na_3Cit$, 0.25 M $Na_2SO_4$) ≈ case 5 (0.1 M $Na_3Cit$, 0.5 M $Na_2SO_4$). Since, an increase in electrolyte concentration may give rise to a corresponding increase in conductivity of membrane layers and thus, a slight increase in potential across the layers. However, this difference is not so appreciable at high current densities if the salt concentrations are close, because, most potential of BP is contributed from the bipolar junction due to the depletion of ions, when water dissociation occurs. So the membrane potential only shows a slight decrease at high salt concentration, as in the case of 1 M $Na_3Cit$ in acid compartment and 1 M $Na_2SO_4$.

### 3.2. Voltage across the cell stack

Cell voltage is an important parameter because it is related to energy consumption associated with the production of an acid and a base based on BP. The voltage drop, which refers to the variation that take place in the ED cell, mainly includes, the Donnan potential at all solution–membrane interface and diffusional potential both in the mono-exchange membrane and in the solution as well as the voltage across a BP [15]. So it is connected with the number of the compartments and the concentration of electrolyte solution in the compartments and thus related with cell configurations. In the previous contributions, we have discussed the effect the cell configuration on the stack voltage [16,17]. Here, we emphasize the effect of salt concentration. Values of the voltage drop based on the current arrangement at a typical current density $I = 100$ mA cm$^{-2}$ and different concentrations are plotted in Fig. 5. It can be noticed that, when a constant current was applied (gavanostatic conditions), the cell voltage drops kept approximately constant, indicating that the water dissociation at this condition approaches to be steady state. When the cell voltages are compared with different electrolyte concentrations, it is interesting to find the values follow the same order as those across a BP, i.e. case 1 (1 M $Na_3Cit$, 1 M $Na_2SO_4$) < case 2 (1 M $Na_3Cit$, 0.5 M $Na_2SO_4$) ≈ case 3 (0.5 M $Na_3Cit$, 0.5 M $Na_2SO_4$) < case 4 (1 M $Na_3Cit$, 0.25 M $Na_2SO_4$) ≈ case 5 (0.1 M $Na_3Cit$, 0.5 M $Na_2SO_4$). It is indicated that, the cell voltage is not only related with the support electrolyte
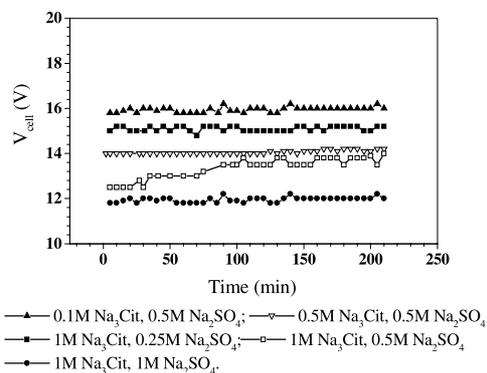
Fig. 5. Time dependence of the voltages across the cell at $I = 100$ mA cm$^{-2}$ for different concentrations.

concentration, but also related with organic salt concentration. However, the support electrolyte Na$_2$SO$_4$ seems to play a decisive role on the voltage because, it is a strong electrolyte while, organic salt is a weak one. A difference of the order of $\sim 4$ V was observed among the cases of different concentrations. This difference is larger than that across a BP because, salt concentration not only affects the membrane potential, but also affects the solution conductivity between the compartments.

### 3.3. Current efficiency

The current efficiency $\eta$ was calculated as Eq. (1) [8]

$$\eta = \frac{(C_t - C_0)VF}{NIt} \tag{1}$$

where $C_0$ and $C_t$ are the concentration of citric acid (acid compartment) at time 0 and $t$, respectively. $V$ is the circulated volume of solution in each compartment, $I$ the current, $F$ the Faraday constant and $N$ is the number of cell triplets ($N = 1$ based on the current set up).

The current efficiency is determined by various time intervals from the beginning and therefore, it is dependent of time. As shown in Fig. 6, the current efficiency
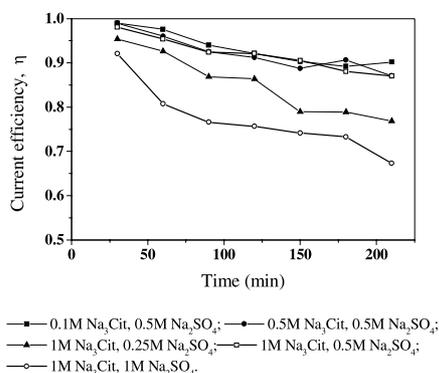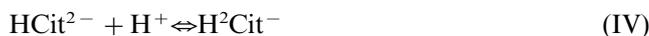


Fig. 6. Current efficiencies for citric acid production vs. time at $I = 100$ mA cm$^{-2}$.

decreases with time, which conforms to the typical trends. At a given time, the current efficiency decrease with increase in the concentration of sodium citrate, as in the case of 0.1, 0.5, 1 M sodium citrate solutions, thereby restricting the possibility of obtaining high concentration of acid and alkali [8].

The trends in the variation of current efficiency with the sodium citrate concentration is easily explained in terms of the ionic transport in the set up and conversion reactions of citric acid as shown in IIIIIIIVVVI.

$$H_2O \Leftrightarrow H^+ + OH^- \tag{I}$$

$$Na^3Cit \Rightarrow Cit^{3-} + 3Na^+ \tag{II}$$

$$Cit^{3-} + H^+ \Leftrightarrow HCit^{2-} \tag{III}$$

$$HCit^{2-} + H^+ \Leftrightarrow H^2Cit^- \tag{IV}$$

$$H^2Cit^- + H^+ \Leftrightarrow H^3Cit \tag{V}$$

Overall reaction:

$$3H_2O + Na_3Cit \Leftrightarrow H_3Cit + 3NaOH \tag{VI}$$

Obviously, the formation of citric acid largely depends on the ionic transport in the BP cell. An increase in sodium citrate concentration can increase the concentration of citrate ions (Eq. (II)), which likely cause a more formation of citric acid due to the less degree of dissociation of the acid as shown in formula (Eqs. (III), (IV) and (V)). Since, the citric acid is a weak electrolyte ($pK_1 = 3.13$, $pK_1 = 4.76$, $pK_1 = 6.40$), experiencing a considerably reduced Donnan exclusion to mono-membrane, the formed acid is easily lost by diffusion into the neighboring compartment through the membrane to that of the acid stream [8]. So, an increase in sodium citrate concentration will reduce the degree of dissociation of citric acid favoring a diffusion of undissociated acid and thus the current efficiency is decreased.

The effect of Na$_2$SO$_4$ concentration on the current efficiency can be obtained by comparing the same sodium citrate concentration, as in the case of 0.25, 0.5, 1 M sodium sulfate solution with 1 M sodium citrate solution. The results are also shown in Fig. 6. It is found that, the current efficiency increases with the concentration of sodium sulfate at low concentration range and then decreases. These results may be explained considering two things. On one hand, an increase in support electrolyte concentration will increase the conductivity in the compartments and decrease the cell voltage as shown in Fig. 5 and thus yield a high efficiency; but on the other hand, an increase in electrolyte concentration may also give rise to the unfavorable factors for the formation of citric acid based on the following considerations.

The production of citric acid with BP can be considered as an exchange reaction between Na$^+$ and H$^+$ as shown in Eq. (VII).
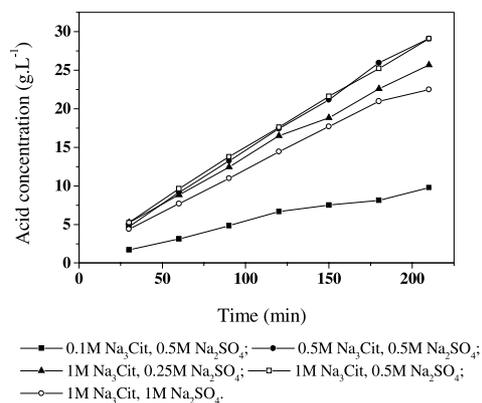
Fig. 7. Time dependence of citric acid concentration in the acid compartment ($I = 100$ mA cm$^{-2}$).

$$Na_3Cit + 3H^+ \Leftrightarrow H_3Cit + 3Na^+ \qquad (VII)$$

An increase in $Na_2SO_4$ concentration will increase diffusion flux of $Na_2SO_4$ from the salt compartment 2 into the neighboring acid compartment through the cation exchange membrane, where sodium ions meet citric acid and increase the degree of dissociation of citric acid. The dissociated proton is easily lost by inter-diffusion with sodium ions through a cation exchange membrane into salt compartment, where they neutralize with hydroxyl ions produced from anionic side of the BP. The concentration of citric acid is then decreased and thus the current efficiency decreases with sodium sulfate concentration. It should be noted that the case of 1 M $Na_3Cit$, 0.5 M $Na_2SO_4$ has a close current efficiency to the case of 0.5 M $Na_3Cit$, 0.5 M $Na_2SO_4$ when different sodium citrate and sodium sulfate concentrations are compared.

### 3.4. Citric acid concentration

As shown in Fig. 7, citric acid concentration varies linearly with time in the acid compartment. From the slope of those plots, the production rates of citric acid can be determined. Obviously, the concentrations of $Na_2SO_4$ and $Na_3Cit$ have little effect on these rates except the case of low $Na_3Cit$ concentration. However, the concentrations of the salts have some effect on the magnitude of acid concentration. As shown in Fig. 7, the acid concentration increases with $Na_3Cit$ concentration before $[Na_3Cit] = 0.5$ M and then keep approximately unchanged, in the considering concentration range. It suggest that for such kind of operation, high acid concentration can not be achieved by increasing the corresponding salt concentration, thereby restricting the possibility of obtaining high concentration of acid as mentioned above from the view of current efficiency. Better operations may be obtained by optimizing the membranes' configurations

and improving the cell structure [8,16]. The effect of $Na_2SO_4$ concentration on the acid concentration is almost the same as that on current efficiency, which supports the former analysis. As observed from Fig. 7, a maximum concentration of acid as high as 30 g l$^{-1}$ may be obtained at the cases of 0.5 M $Na_3Cit$–0.5 M $Na_2SO_4$ and 1 M $Na_3Cit$–0.5 M $Na_2SO_4$ before time = 200 min, thereby providing the technical feasibility of converting citric acid from sodium citrate, using BP. A higher value for acid concentration can be achieved if the recirculation time is longer. In comparison with the conventional fermentation process, the new process can produce acid citrate with a relative high purity due to the high selectivity of membranes and decrease the discard of solid wastes to a great extent because, lime neutralization and the followed precipitation were avoided. Since, citrate has a relative high solubility in water, e.g. 1.65 kg/kg water at 25 °C [1], in our experimental process, no scaling phenomena was observed on the membranes.

### 3.5. Energy consumption

The energy consumption $E$ (kW h kg$^{-1}$) was calculated by extrapolating the results for the production of 1 kg of citric acid based on Eq. (2)

$$E = \int \frac{UI\mathrm{d}t}{C_t VM} \qquad (2)$$

Here, $U$ is the potential across the cell stack ($V$), $M$ is the molar weight of citric acid (192 g mol$^{-1}$). The results, shown in Fig. 8, indicate that the energy consumption increases with the current density. For the comparisons between different salt concentration, the trends are just opposite to those for current efficiency. For example, the maximum energy assumption corre-
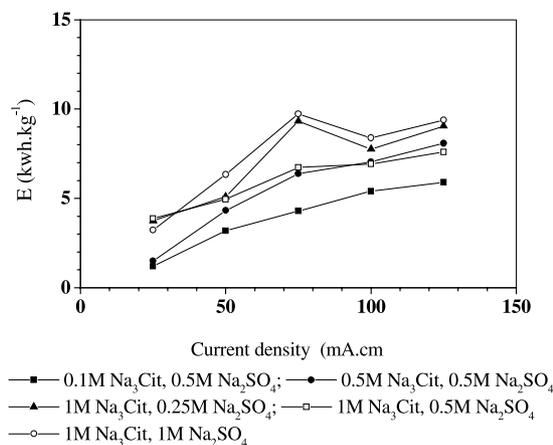


Fig. 8. Energy consumption for the production of citric acid production vs. current density.

sponds to the lowest current efficiency at the case of 1 M $Na_3Cit$–1 M $Na_2SO_4$, while the minimum energy consumption to the lowest current efficiency at case of 0.1 M $Na_3Cit$–1 M $Na_2SO_4$. The results may also be explained by the ionic transport and exchange, as described before.

## 4. Conclusions

1. ED with BP provides a convenient way to produce citric acid from its salt solution. In comparison with the conventional fermentation process, the new process can produce acid citrate with a relative high purity due to the high selectivity of membranes and decrease the discard of solid wastes to a great extent because, lime neutralization and the followed precipitation were avoided.
2. Both the sodium citrate concentration and sodium sulfate concentration have an effect on such a process. The trends can be explained in terms of ionic transport and exchange reaction between protons and sodium ions. In the practical operations, it suggests the optimum concentration ranges 0.5–1.0 M for sodium citrate and 0.25–1.5 M for sodium sulfate from the considerations of energy consumption, current efficiency and acid concentration.
3. A maximum concentration of acid as high as 30 g $l^{-1}$ has been obtained at the cases of 0.5 M $Na_3Cit$–0.5 M $Na_2SO_4$ and 1 M $Na_3Cit$–0.5 M $Na_2SO_4$ and a recirculation time of 200 min, thereby providing the technical feasibility of converting citric acid from sodium citrate using BP.
4. The above results provide a basis to conduct a large scale experiments with fermentation broth.

## Acknowledgements

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