

Review

Application of electrodialysis to the production of organic acids: State-of-the-art and recent developments

Chuanhui Huang, Tongwen Xu*, Yaping Zhang, Yanhong Xue, Guangwen Chen

Laboratory of Functional Membranes, School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, PR China

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Abstract

The production of organic acids needs innovations to keep up with the development of modern chemical and biochemical industries. Electrodialysis (ED) may be the key innovation. Accordingly, based on a summary on the related literature, we compiled an introduction to the production of organic acids by using ED, which includes conventional electrodialysis (CED), electrometathesis (EMT), electro-ion substitution (EIS), electroelectrodialysis (EED), electrohydrolysis with bipolar membranes (EDBM), electrodeionization (EDI), and two-phase electrodialysis (TPED). We hope that, apart from the separation and conversion of organic acids or organic salts, ED can promote the comprehensive utilization of renewable resources and contribute to the sustainable development of humankind.

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Keywords: Electrodialysis; Organic acids; Ion-exchange membrane; Bipolar membrane; Cleaning production

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* Corresponding author. Tel.: +86 551 3601587; fax: +86 551 3601592.
E-mail address: twxu@ustc.edu.cn (T. Xu).

1. Introduction

Organic acids are those organic compounds which are acids, and they include carboxylic acids, enols, phenols, sulfonic acids, mercapto-compounds, and phosphonic acids. They have been widely used in foods, beverages, pharmaceuticals, cosmetics, detergents, plastics, resins, and other biochemical or chemical products (Table 1 [1–3]), and thus have a close relationship with human's daily life.

There are two prevailing methods for the production of organic acids: fermentation and chemical synthesis. From the viewpoint of sustainable development and human health, the former is preferred to produce the organic acids which are metabolic intermediates or products. First, fermentation uses renewable resources as the feedstock, such as silage, grains, syrups, molasses, and cheese whey. Not only is the feedstock supply guaranteed, but also resource recycling is achieved in the biosphere. Second, the products from fermentation have a higher safety degree, which is significant to human health. Third, some organic acids should not or are difficult to be produced

via chemical synthesis. Taking lactic acid for an example, the chemical synthesis produces a racemic mixture of lactic acid (L- and D-forms) while fermentation can selectively synthesize the desired stereospecific lactic acid [4]. Notably, over taking D- or DL-lactic acid will cause metabolism disorder.

Whether it is fermentation or chemical synthesis, separation, concentration, and purification are necessary for product preparation. More processes follow fermentation since the broth has various ingredients to separate. The related traditional techniques include precipitation and acidification, extraction, crystallization, distillation, ion-exchange, and adsorption. However, it becomes difficult for them to meet the requirements of modern chemistry, which is characterized by “design for the environment (DFE)” and “green chemistry” [5]. Precipitation and acidification are notorious for the solid pollution—CaSO₄ sludge. Solvent extraction is handicapped by undesirable distribution coefficients and environmental problems due to the use of hazardous solvents [6]. Crystallization is unfavorable due to its low yield, high costs for chemical use, and waste discharge. Direct distillation has high-energy consumption and in some

Table 1
Properties and main uses of some organic acids

Acid	Molecular weight (g/mol)	Electrical conductivity (mS/cm)	Dissociation constant			Main uses	References
			p <i>K</i> ₁	p <i>K</i> ₂	p <i>K</i> ₃		
Formic acid	46.03	5.18 ^a	3.752			Used in dyeing and finishing textiles and paper and in the manufacture of fumigants, insecticides, and refrigerants	[1,3,36]
Acetic acid	60.05	1.32 ^a	4.756			Vinegar; a solvent in the manufacture of rubber, plastics, acetate fibers, pharmaceuticals, or photographic chemicals	[1,3]
Propionic acid	74.08	1.00 ^a	4.874			Used as in the form of its propionates as a mold inhibitor in bread and as an ingredient in perfume	[1,3]
Lactic acid	90.08	1.32 ^b	3.858			Used in foods and beverages as a flavoring and preservative, in dyeing and textile printing, and in pharmaceuticals; synthesis of biodegradable plastics	[1,3,60]
Gluconic acid	196.16	Not available	3.86			Food additive; acidity regulator, chelating agent	[3,26]
Oxalic acid	90.04	2.97 ^a	1.271	4.266		Bleach and rust remover	[2,3]
Malic acid	134.09	Not available	3.460	5.050		Used as a flavoring and in the aging of wine	[2,35]
Itaconic acid	130.10	Not available	3.85	5.45		Used for preparing deodorants, SBR latex, medicine, cosmetics, lubricants, and herbicides	[3]
Tartaric acid	150.09	7.03 ^c	3.04	4.87		Used to make cream of tartar and baking powder, as a sequestrant, and in effervescent beverages and photographic chemicals	[3]
Salicylic acid	138.12	Not available	2.98	12.38		Used in making aspirin, as a preservative, and in the external treatment of skin conditions such as eczema	[3,52]
Citric acid	192.12	5.40 ^a	3.128	4.761	6.396	A flavoring agent for foods and beverages; water conditioner; cleaning and polishing agent; chemical intermediate. Substitute for phosphoric salts used in detergents	[2,3,53]
Ascorbic acid	176.13	Not available	4.30	11.82		Antioxidant; medicine (preventing scurvy)	[3,50]
Glutamine	146.14	Not available	2.13	4.31	9.76	Used in medicine and biochemical research and as a feed additive	[3,17]

^a 18 °C, aqueous, 1N.

^b 18 °C, aqueous, 0.1N.

^c 15 °C, aqueous, 1N.

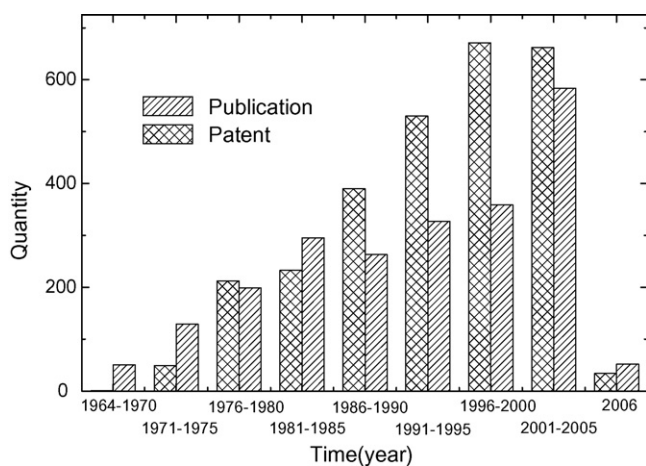


Fig. 1. Chronology of ED documents. Source: www.scopus.com [search settings: TITLE-ABS-KEY (electrodialysis). Search date: 16 August 2006].

cases will cause product transformation, such as the polymerization of lactic acid [7]. As for ion-exchange, a great amount of acid, base and water are needed to rehabilitate the ion-exchange resins. Furthermore, salt formation cannot be avoided because the acid's anion and the base's cation have no other outlets. Adsorption also has its disadvantages such as short lifetime of adsorbents, low capacity and additional filtration. Naturally, the techniques with a stronger economic and environmental competence are needed for the production and downstream processing of organic acids.

Membrane technologies have been proving their advance in the fields of separation and purification. As one membrane technology, electrolysis (ED) has attracted much attention from the academia and industry due to its diversity, sophisticated functions, and technological compatibility. Fig. 1 illustrates the chronology of ED documents and confirms the increase in efforts from the academia on ED research. When it comes to the separation and production of organic acids, ED may be the most competitive technology because of its predominance in simultaneous supply of H^+ and OH^- /alkoxide ions without salt introduction or discharge [8], salt conversion, technological symbiosis, and resource utilization.

Accordingly, in this paper, the role that ED plays in the production of organic acids was illustrated on the basis of a summary on the related literature. Hopefully, the following discussions can be useful reference for researchers, entrepreneurs, and administrators.

2. General description of ED

In the past century, ED kept ramifying after it came into being. At the present, this ED family comprises conventional electrodialysis (CED), electrometathesis (EMT), electro-ion substitution (EIS), eletro-ion injection-extraction (EIIE), electro-electrodialysis (EED), electrohydrolysis with bipolar membranes (EDBM), electrodeionization (EDI), and two-phase electrodialysis (TPED) [9–12]. In spite of its diversity, ED can be summarized as a type of technology which arranges ion-exchange membranes (cation-selective, anion-

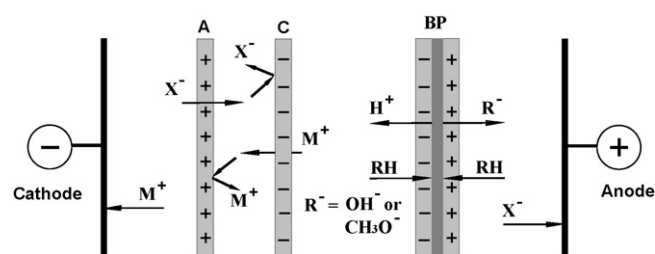


Fig. 2. Schematic representation of electrodialysis. BP: bipolar membrane; A: anion-selective membrane; C: cation-selective membrane; M^+ : cation; X^- : anion; H^+ : hydrogen ion; OH^- : hydroxide ion; CH_3O^- : methoxide ion.

selective and/or bipolar membranes) alternately in a direct current field (Fig. 2). In particular, there are at least four elements complementary for ED applications:

- (1) *Direct current supply*. It proves an effective means to reinforce ion transport, i.e., cations and anions migrate towards the cathode and anode, respectively. Furthermore, the migration rate of ions can be controlled by adjusting the current density.
- (2) *Electrodes*. The oxidation/reduction reactions on the cathode and anode realize the transformation from ionic conduction to electron conduction, and thus provide the original driving force for ion migration. Generally speaking, the electrode applied in ED is inert and plate-shaped. Naturally, gas bubbles are formed on the interface of the solvent and electrode, i.e., H_2 and O_2 in the case of water electrolysis, and H_2 , CO_2 , C_2H_6 , etc., in the case of alcohol electrolysis. As concerns the metallic redox reactions, metal deposition is likely to occur on the surface of cathodes.
- (3) *Ion-exchange membranes*. There are three types of ion-exchange membranes which can be applied in ED separately or in combination. As two of the three, cation- and anion-selective membranes are well known for hindering the passage of co-ions (anions and cations, respectively) due to the Donnan repulsion. The other type of ion-exchange membrane is the bipolar membrane, which is a composition of a cation-selective layer and an anion-selective layer. It can be considered as a combination of a cation-selective membrane and an anion-selective one, but it has distinctive functions from those mono-polar membranes. Under reverse potential bias, bipolar membranes can realize the dissociation of solvent molecules. At the present, there are only two kinds of solvents reported to dissociate in bipolar membranes: water (H_2O) and methanol (CH_3OH) [13]. They split into H^+ and OH^- , and H^+ and CH_3O^- , respectively. It is noteworthy that the solvent splitting in bipolar membranes has some preponderancies over solvent electrolysis, such as no gas or byproduct generation, lower voltage drop, maximal energy utilization, space-saving, easier installation and operation, and less initial investment.
- (4) *Solvents and electrolytes*. Solvents make a continuum for ion transport by filling the space between the electrodes and required membranes, while electrolytes are the current carriers between the cathode and anode. The solubility of salts or electrolytes in solvents is critical to the electrical resis-

Table 2
ED applications

Technique	Main functions	Applications	Competing techniques	References
CED	Demineralization and concentration	Desalination of brackish or seawater; boiler water treatment; blood purification; demineralization and concentration of industrial feeds or effluents; preparation of SiO ₂ or Al ₂ O ₃ sol	Reverse osmosis; ion-exchange; chemical synthesis	[9,11,14]
EMT	Double composition	Preparation of malic acid, methoxide, and tartaric acid	Chemical synthesis	[9]
EIS	Ion substitution	Preparation of sodium dihydrogenphosphate	Chemical synthesis; ion-exchange	[9]
EIE	Ion injection-extraction	Cyclodehydrohalogenation of dibromopropanol	Chemical synthesis; ion-exchange	[9]
EED	Electrolysis and ion substitution	Chlor-alkali production; electrohydrodimerization of acrylonitrile into adiponitrile; electroreduction of salicylic acid into saligenin	Chemical synthesis; ion-exchange; electrolysis	[9,10]
EDBM	Acid and/or base/alkoxide production; acidification and alkalization	Production or recovery of inorganic or organic acids and/or bases; salt conversion; separation and concentration of ionic species; stabilization of beverages; organic synthesis	Electrolysis; ion-exchange; precipitation and acidification; adsorption; crystallization, extraction	[9–11,14]
EDI	Deionization	Preparation of ultrapure water	Ion-exchange	[10,11]
TPED	Extraction; solubility increasing; accelerated ion migration	Production of low water-soluble organic acids; separation of organic acids from fermentation broths	Electrophoresis; extraction; EED; precipitation and acidification	[12,52,54]

tance and thus the energy consumption of ED stacks, and it also affects the operation stability (including membrane fouling and pipe erosion). Notably, some solvents are the feedstock needed for membranes to function, i.e., methanol for the alcohol splitting in bipolar membranes.

The above four complementary elements provide ED with some basic features, such as reinforced ion migration, membrane permselectivity, solvent electrolysis and/or splitting, and liquid-phase operation. Through the selection and combination of different membranes and solvents, ED can be used for demineralization and concentration of salt-containing solutions, acid and/or base/alkoxide production or regeneration, acidification and alkalization, ion substitution, double composition, ion injection-extraction and organic syntheses (Table 2 [9–11,14]).

3. Application of ED to the production of organic acids

Most of the ED techniques aforementioned have found their applications in organic acid production, and the roles they played are illustrated as follows.

3.1. CED: demineralizing or concentrating organic acids or organic salts

CED is a kind of ED technique whose repeating unit consists of a cation-selective membrane, an anion-selective membrane, and two compartments. The typical function of CED is simultaneous dilution and concentration of salt-containing solutions, and this ED technique was often used to treat brackish or seawater before reverse osmosis took its place.

When it comes to organic acid production, CED has been used to demineralize or concentrate organic acids or organic salts. Specifically, the CED stack as shown in Fig. 3a has been reported to demineralize lactic acid [15], glutamine [16,17], glycine [18],

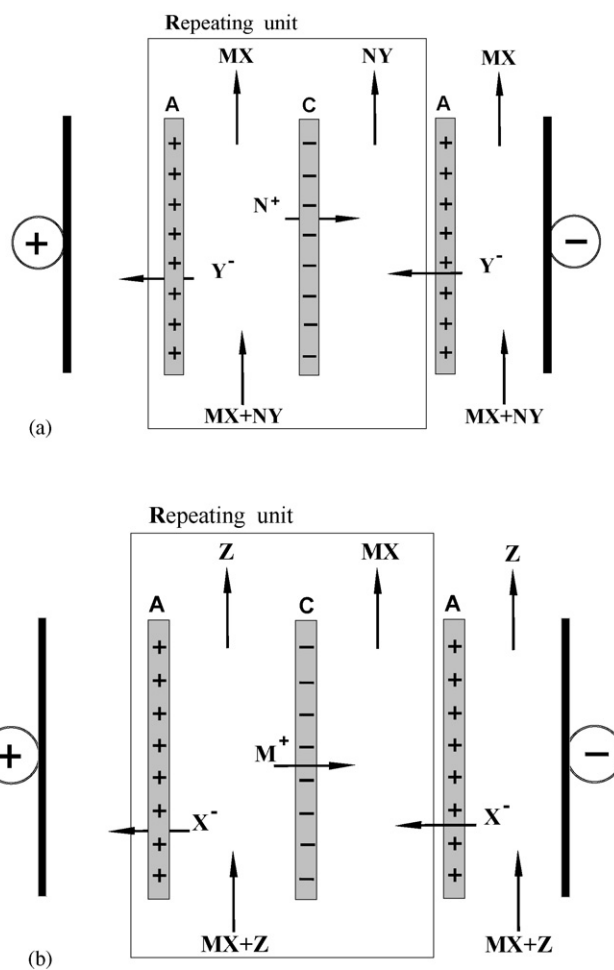


Fig. 3. Schematic representation of the CED applied to (a) demineralize or (b) concentrate organic acids or organic salts. MX: organic acid or salt; NY: inorganic salt; Z: neutral substances or low concentration of inorganic salts.

and D- α -p-hydroxyphenylglycine [19]. Fig. 3b illustrates the stack reported to concentrate lactate [20–24], lysine [25], glycine [18], gluconate [26], propionate [27], pyruvate [28], and formic acid [29]. The efficiency of demineralization or concentration mainly depends on counter-ion competence, which increases with the ion quantity and mobility. In the case of demineralization, it is better to acidify the feed so that most of organic anions can exist in the form of acid molecules and stay in the feed, and more inorganic anions can migrate into the adjacent compartment. As far as amino acids are concerned, a greater efficiency can be achieved if the feed pH is adjusted to the isoelectric point of the amino acid. In the case of concentration of organic acids or organic salts, the opposite measures can be taken to achieve a higher efficiency.

As for the separation of organic acid mixtures, counter-ion competence plays a critical role in ion transport. Moon et al. has investigated the desalting and separation of binary and quaternary acid mixtures, and the related acids were formic, acetic, succinic, and lactic acids [30]. They found that the separate factor increased with the difference in ionization degree, ion mobility, molar concentration, and molecular dimensions. Accordingly, formate anions are the most preferential current carriers and lactate anions the least while succinate and acetate anions are difficult to separate from each other.

3.2. EIS: producing organic acids via H^+ substitution

EIS is a kind of ED technique whose repeating unit consists of two adjacent cation-selective (or anion-selective) membranes, one anion-selective (or cation-selective) membrane, and three compartments. It can realize the substitution between ions of the same sign. Fig. 4 shows the EIS stack used to produce lactic acid [31]. The H^+ needed for ion substitution was supplied by an additional feed stream (H_2SO_4). The current efficiency can reach more than 100% at the beginning due to the H^+/M^+ Donnan dialysis, but more M^+ in the acid stream will compete with H^+ and thus decrease the efficiency. However, M^+ competition can be suppressed by using a cation-selective membrane with higher H^+/M^+ permselectivity.

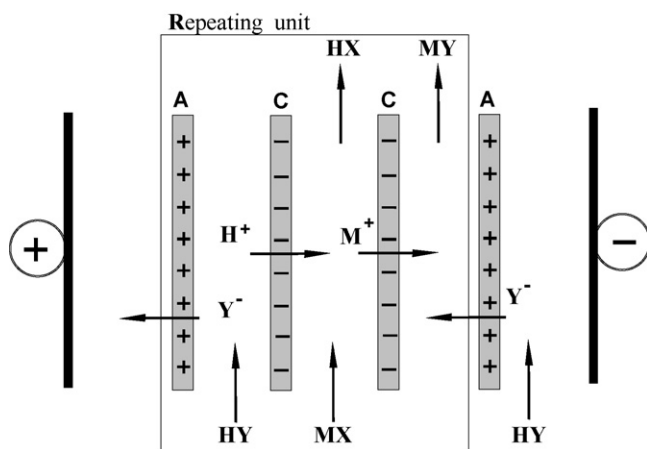


Fig. 4. Schematic representation of the EIS applied to produce organic acids. HY: inorganic acid.

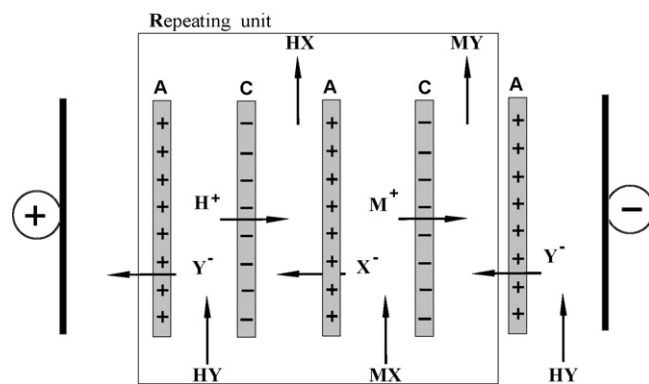


Fig. 5. Schematic representation of the EMT applied to produce organic acids.

3.3. EMT: producing organic acids via double composition

EMT is a kind of ED technique whose repeating unit consists of four alternately arranged mono-polar membranes (two anion-selective and two cation-selective), and four compartments. It has two kinds of feed streams and outputs, and can realize double composition reactions most of which hardly occur in other conditions than in ED systems. EMT (see Fig. 5) has been applied to produce citric acid [32] and lactic acid [6,33]. Inorganic acids (for example, HCl and H_2SO_4) are necessary for the conversion of organic salts into organic acids, and the formed inorganic salts should be used for process recycling or fertilizer preparation, or else it will pollute the environment if discharged without treatment.

3.4. EED: producing organic acids via electrode reactions

EED is a kind of ED technique which has no repeating units and where electrode reactions play a critical role in feed treatment. The cathode or anode reaction either provides reactants or consumes the ingredients in feed. As concerns organic acid production, the electrode reactions provide H^+ or OH^- for the acidification or ionization of organic anions. Fig. 6a presents the mono-membrane EED stack applied to recover organic acids (butyric, valeric, adipic, caproic, and oxalic acids) [34], and Fig. 6b the multi-membrane EED stack to produce L-malic acid [35].

3.5. EDBM: producing organic acids via the water splitting in bipolar membranes

EDBM is a kind of ED technique which is characteristic of the solvent (water or methanol, hitherto) splitting in bipolar membranes. It has attracted more attention from the academia due to its technical advance, economic competence, and environmental benignity [8]. When applied to organic acid production, EDBM can overcome the disadvantages which are inherent in CED, EIS, EMT, and EED, i.e., extra input of inorganic acids as H^+ source, salt pollution if discharged without treatment, or a great proportion electrode reactions account for in energy consumption and process cost. Furthermore, EDBM can achieve the

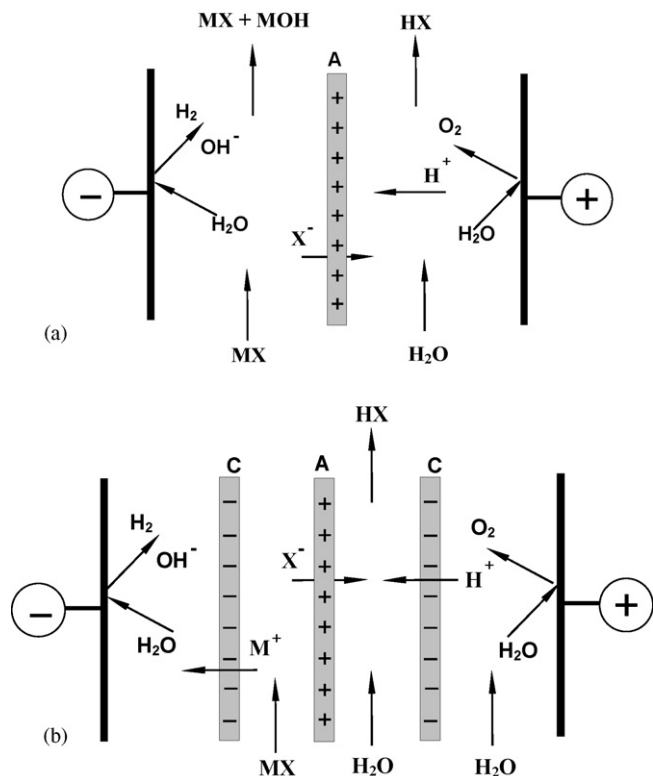


Fig. 6. Schematic representation of the EED applied to produce organic acids. (a) Mono-membrane system and (b) multi-membrane system.

utmost utilization of resources by supplying H^+ or OH^- in situ and without any salt introduction or secondary pollution.

This technique has been used for the production of formic acid [36], acetic acid [37], propionic acid [38], lactic acid [4,7,21,23,24,39–41], citric acid [42–46], *p*-toluenesulfonic acid [47], salicylic acid [48], itaconic acid [49], Vitamin C, gluconic acid [40,41,50], and some other amino acids [51]. There are three main cell configurations (Fig. 7a–c) feasible for the production of organic acids. Generally, the three-compartment EDBM can be applied to produce strong or weak organic acids, but measures should be taken to decrease the electrical resistance when producing weak organic acids [47]. As for the two-compartment EDBM, it has a less energy consumption than the three-compartment one. The two-compartment EDBM via H^+/M^+ substitution (Fig. 7b) is unfavorable for strong acid production since more free H^+ will compete with M^+ and decrease the current efficiency. The two-compartment EDBM via OH^-/X^- substitution (Fig. 7c) has a greater energy consumption than that via H^+/M^+ substitution due to the lower mobility of organic ions. Nonetheless, some neutral impurities can be kept from the product stream in the three-compartment EDBM and the two-compartment EDBM via OH^-/X^- substitution.

Notably, most of the works reported were conducted with sodium organic salts as the model subject, and this brings out something to be desired in EDBM technology for the application to organic acid production. For one thing, fermentation liquors have various organic ingredients, but EDBM does not possess selectivity for the desired organic acid. For another, some organic acids, such as salicylic acid, have a low solubil-

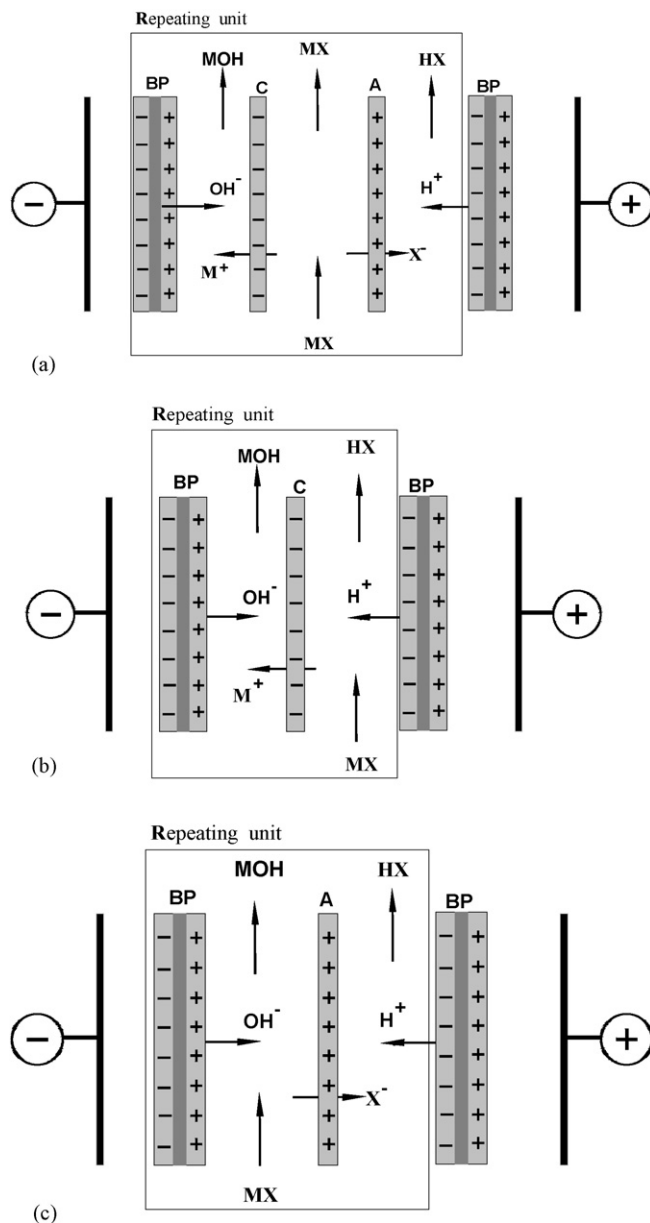


Fig. 7. Schematic representation of the EDBM applied to produce organic acids. (a) Three-compartment EDBM, (b) two-compartment EDBM via H^+/M^+ substitution and (c) two-compartment EDBM via OH^-/X^- substitution. BP: bipolar membrane; MX: organic salt. X^- : organic anion.

ity in water [52], which is another limitation to the application of EDBM. Therefore, in order to achieve the technological advance, some improvements are expected to be made on the selective extraction when using EDBM.

3.6. EDI: concentrating organic acids organic salts by using ion-exchange resins as the bridge over current carriers

Using ion-exchange resins as the bridge over current carriers is a strategy to decrease the electrical resistance of dilute solutions and thus the energy consumption of the ED stack, which is the most important principle for EDI to prepare ultrapure water.

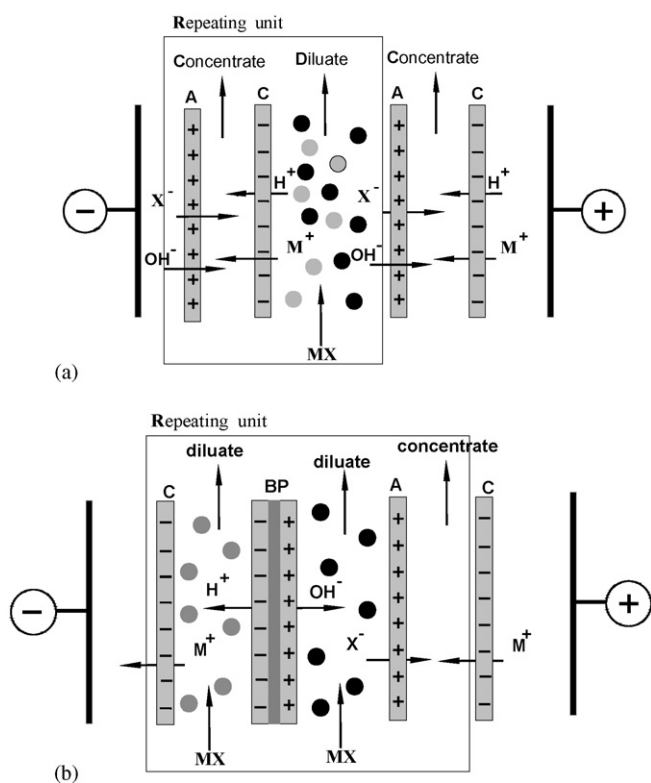


Fig. 8. Schematic representation of the EDI applied to concentrate organic acids or organic salts. (a) Conventional EDI and (b) the EDI using bipolar membranes. (○) cation-exchange bead; (●) anion-exchange bead; MX: organic acid or organic salt.

This strategy can also be adopted for the treatment of low concentrations of organic acids by using CED. Fig. 8a shows the EDI applied to the production of citric acid [53]. The ion-exchange resins can be somewhat rehabilitated via the water splitting induced by concentration polarization. However, the rehabilitation of resins and current utilization can be improved by using EDI with bipolar membranes (Fig. 8b), because (1) the water splitting in bipolar membrane has a much higher efficiency, and (2) the generated H^+ and OH^- are kept from recombination due to the separation by mono-polar membranes [8].

3.7. TPED: producing low water-soluble organic acids by using organic solvents

As concerns low water-soluble organic acids and organic salts, they will form solid particles or suspending droplets if fed into ED steams, and it will lead to (1) membrane fouling, (2) pump erosion, (3) low productivity, and (4) unstable operation. Naturally, this problem can be solved by choosing specific organic solvents, which can increase the solubility of organic materials. That is one of the roles organic solvents play in TPED. Fig. 9a shows the two-phase EIS (TPEIS) used for the production of aliphatic acids or salicylic acid [52,54]. The organic salts were dissolved in a 50% (v/v) water–ethanol solution. The ethanol used can increase the solubility of organic acids or organic salts, but the ethanol/water rate should be kept below a certain value (for example, 50%, v/v) because excess ethanol

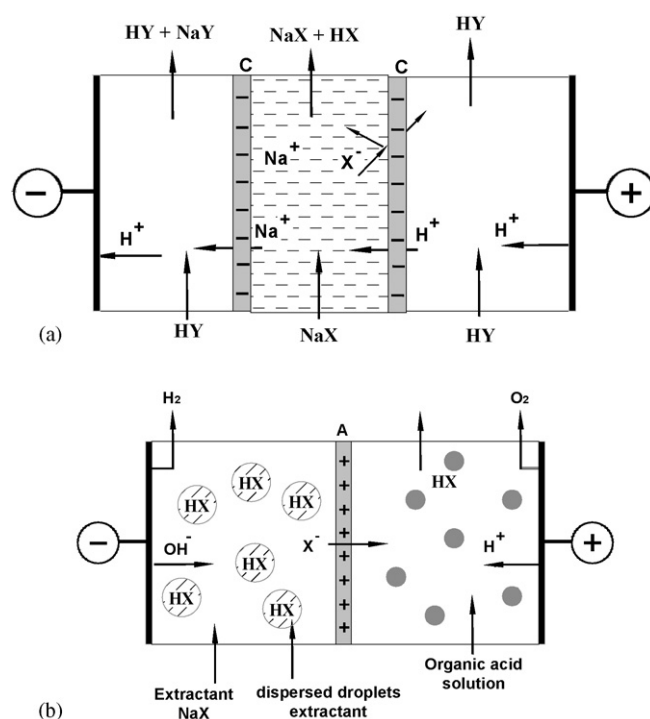


Fig. 9. Schematic of the TPED applied to produce organic acids. (a) Two-phase EIS: producing low water-soluble organic acids and (b) the two-phase EED coupled with back-extraction. NaX: sodium organic salt; (□) aqueous–organic phase; (○) or HX: organic acid; (▨) organic phase; (□) aqueous phase.

will compete with organic anions for the H^+ which migrates from adjacent compartments. Furthermore, the substitution of water with ethanol leads to an increase in the electrical resistance of the stack. As for the compartments beside the feed compartment, they were filled with water. Firstly, water can dissolve more inorganic supporting electrolytes (inorganic acids) than ethanol and keep the electrical resistance under ease control. Secondly, the organic–aqueous interface is favorable for the suppression of co-ion (organic anions) leakage since organic anions are preferentially distributed to the aqueous–organic or organic phase. Last but not least, the organic–aqueous interface favors the reduction of water electro-osmosis and osmosis.

Another role organic solvents play in TPED is that some organic solvents can act as extractants and bestow ED the selectivity for desired reactants. Fig. 9b illustrates the production of citric acid by using two-phase electro-electrolysis (TPEED) coupled with back-extraction [12]. Citric acid was selectively extracted from the fermentation broth by using the organic extractant and back-extracted by using a sodium citrate solution after fed into the cathode compartment. The acid molecules were ionized at the alkali pH, which was adjusted by the OH^- from the cathode reaction. The formed citric anions migrated into the anode compartment and formed citric acid after combining with the H^+ from the anode reaction. This process realizes the simultaneous extraction, back-extraction, separation and concentration of citric acid but still has acceptable energy consumption.

Theoretically, organic solvents can be used in other ED techniques, but they were seldom reported for the production of organic acids.

4. Process integration and optimization

Most of the research aforementioned used a pure solution of organic salts or organic acids as the subject for feasibility experiments, but the practical feeds from chemical synthesis or fermentation are more complicated. Auxiliary treatment and process integration are needed to realize the production of organic acids from industrial feeds and the utmost utilization of resources.

4.1. Pretreatments

To ensure stable operation and process performance, the feed solution needs treating before pumped into the ED stack. When designing pretreatments, one has to consider the specific conditions of the feed. Firstly, press filtration and ultrafiltration [21,22] are often used to remove particles or colloids (bacteria, cellulose, proteins, or suspended solid chemicals) and keep the ED stack free from serious membrane fouling, pipe jam or pump erosion. The solid residue filtrated from fermentation broth can be further processed for the use in agriculture. Secondly, activated carbon [24] is preferentially employed to clear up coloring matters in case that they foul the membranes or render the product unfavorable appearances. Thirdly, chelating resins [55,56] are chosen to selectively remove multivalent inorganic ions (especially, Ca^{2+} , Mg^{2+} , Ba^{2+} , Mn^{2+} , Zn^{2+} , Fe^{3+} , and Sr^{2+}) [21,56] in order to prevent scale formation. Naturally, hydrodynamic conditions should be improved in order to suppress concentration polarization, which may result in local supersaturation of solutes.

4.2. Inward integration: CED and EDBM

CED and EDBM are good at concentrating and converting organic salts, respectively, but the former often has a secondary salt pollution and the latter suffers from high cost of bipolar membranes (3–10 times the cost of mono-polar membranes) and high energy consumption due to the low electrical conductance of bipolar membranes when immersed in dilute solutions. If the concentrate from CED is fed into EDBM, these two processes can achieve a synergic effect on organic acid production and may decrease the process cost, which is especially true for the treatment of organic acids with a high molecular weight ($>200 \text{ kg kmol}^{-1}$). Novalic et al. replaced a three-compartment EDBM with a CED plus a two-compartment EDBM (via H^+/Na^+ substitution) [40] and achieved a process with a lower cost for the production of gluconic acid or citric acid. However, organic acid production by only using EDBM may benefit from the zero investment on CED though EDBM has a higher energy consumption [4]. Moreover, the procedures can be further simplified after deleting the measure taken for multi-valent ion removal if using the cation-selective membranes with selectivity for mono-valent ions. Besides, the effluent (glucose, calcium, magnesium, etc.) from EDBM can be reused for fermentation after simply processing. Naturally, the process optimization can only be made on the basis of industrial-scale applications.

4.3. Outward integration: ED and fermentation

ED, especially EDBM, cannot only produce organic acids from fermentation broth, but also benefit fermentation processes by eliminating product inhabitation and ensuring pH stabilization. Some works have been reported to integrate ED and fermentation. Li et al. invented an electrokinetic bioreactor to enhance lactic acid fermentation and product recovery [39]. In the bioreactor, the fermentation was conducted in the alkali compartment of a three-compartment EDBM, which was equipped with a pH sensor and current control system. The OH^- generated in bipolar membranes can ionize the formed lactic acid and thus keep the broth pH from decreasing. Accelerated by direct current field, the lactic anions migrated across the anion-selective membrane into the acid compartment and thus product inhabitation was alleviated. This process has a high integration degree, but the operation is unstable since it is difficult to keep membranes from being fouled in a fermentation broth and have a higher current efficiency in a system with so many competing anions. Up to now, the more feasible strategy is to integrate ED with fermentation by external auxiliary treatment. This integration in the production of organic acids is called electro dialysis fermentation (EDF). In EDF, the broth is fed into ED in batch or continuously after pretreated as aforementioned, and the effluent is recycled to fermentation. In fact, the loss of water and glucose in ED changes with the ever-changing feed composition, so the effluent needs more control before recycled to the broth. This kind of post-treatments have been reported in literature [57–60], and include applying a level meter, pH controller, and glucose controller.

5. Process economics

Process performance and cost are admittedly the key factors for the industrialization of most processes. As far as environmental benignity is concerned, it is often neglected or not paid enough attention to. However, it will add to the competence of industrial techniques as people value more about life quality, unrenewable resources charge more, and the government undertakes more stringent control over environmental pollution and resource waste.

5.1. Process performance and cost

Table 3 illustrates the process performance and cost for some ED applications in the production of organic acids. The data were directly excerpted from the literature and most of them focused on process performance. As for process cost, it was neglected or difficult to be assessed in most reported works since the experiments were carried out on a laboratory scale. Even in the few works with process cost analyzed, the cost for extra feed streams and secondary pollution control was seldom taken into calculation of the total process cost. That may affect the decision when one selects the better process for organic acid production, and is unfavorable for the implementation of environmental protection.

Table 3
Process performance and cost for ED applications

Application	Scale	ED process characteristics	Economic estimation	References
Production of citric acid	Pilot scale	(Two-compartment EDBM) BM area: 0.004 m ² ; current density: 1000 A/m ² ; current efficiency: 70%; acid concentration: 30 g L ⁻¹	EC: 2–5 kWh/kg acid	[42–44]
Concentration of citric acid	Pilot scale	(EDI) membrane effective area: 1500 cm ² ; current density: 5 mA cm ⁻² ; current efficiency: 40–90%; feed concentration: 2000 ppm; final concentrate concentration: 60,000 ppm	EC: 1.16 kWh/t of feed solution	[53]
Concentration of lactate	Lab scale	(CED) membrane effective area: 180 cm ² ; current efficiency: 81–82%; initial dilute concentration: 85.8 g L ⁻¹ ; final concentrate: 175 g L ⁻¹ ; duration: 220 min	EC: 0.21–0.22 kWh/kg of sodium lactate	[21]
Production of lactic acid	Lab scale	(Three-compartment EDBM) current density: 75 mA cm ⁻² ; current efficiency: 80.8–83.7%; initial lactate: 100–150 g L ⁻¹	EC: 0.54–0.71 kWh/kg of lactate	[23]
Desalination of glutamine	Lab scale	(CED) membrane effective area: 98 cm ² ; pH control: 5.6 ± 0.5; current density: 20.4 mA cm ⁻² ; current efficiency: 81%; glutamine recovery: 78.1%; salt removal ratio: 95%; residual sulfate concentration: 3.0 g L ⁻¹ ; duration: 5 h	EC: 1.95 kWh/kg of sulfate	[17]
Recovery of gluconate	Lab scale	(CED) membrane effective area: 200 cm ² ; current efficiency: 79–88%; gluconate maximum concentration: 30% (v/v)	EC: 0.83 kWh/kg of gluconate	[26]
Production of gluconic acid	Lab scale	(Three-compartment EDBM) membrane effective area: 200 cm ² ; current efficiency: 70–80%; acid maximum concentration: 45% (v/v)	EC: 1.28 kWh/kg of gluconic acid	[26]
Recovery of D-α-p-hydroxyphenylglycine	Lab scale	(CED) membrane effective area: 200 cm ² ; feed: 0.111 M amino acid + 1.333 M (NH ₄) ₂ SO ₄ + 0.687 M NaH ₂ PO ₄ ; salt removal rate: 70%; amino acid recovery: 85%	No information available	[19]
Recovery of an amino acid	Industrial plant aqualytics system	(Three-compartment EDBM) membrane area: 3 m × 180 m; BM lifetime: 2 years; concentration of organic acid: 4–6 M; time of production: 8000 h/year	No information available	[41]
Production of amino acids	Lab scale	(Two-compartment EDBM) initial concentration: 15–18 wt.% (Na–amino acid); membrane effective area: 400 cm ² ; current density: 40–100 mA cm ⁻² ; current efficiency: 85–97% (Na ⁺); product concentration: 8.2–20.7 wt.%	No information available	[51]
Concentration of lysine	Lab scale	(CED) initial concentration: 0.25 mol L ⁻¹ (lysine–HCl); membrane effective area: 7.07 cm ² ; product flux: 19.8 mol m ⁻² h ⁻¹ ; current efficiency: 74.1% (at 75 mA cm ⁻²)	EC: 2–4.6 kWh/kg of lysine (at 25–75 mA cm ⁻²)	[25]
Concentration of glycine	Lab scale	(CED) initial concentration: 0.1 mol L ⁻¹ (glycine), 0.01 mol L ⁻¹ (sucrose); separation factor: 10–40	No information available	[18]
Concentration of formic acid	Lab scale	(CED) membrane effective area: 20 cm ² ; current efficiency: 90–250% (molecular association)	No information available	[29]
Regeneration of formic acid	Lab scale	(Three-compartment EDBM) mean current efficiency: 80%; current density: 500 A/m ² ; Acid concentration: 7 mol/L	EC: 2.6 kWh/kg of acid	[36]
Concentration of propionate	Lab scale	(CED) membrane effective area 72 cm ² ; current density: 20–40 mA cm ⁻² ; conversion ratio: 95%; current efficiency: 98%	EC: about 0.22–0.35 kWh/kg of sodium propionate	[27]
Production of octanoic acid	Lab scale	(TPEIS) membrane area (cm ²): 41; initial composition: 0.5 mol L ⁻¹ sodium octanate in a water–ethanol (1:1) solution; current density (A m ⁻²): 100; conversion rate: 62% (3 h)	No information available	[52]
Recovery of organic acids (butyric, valeric, adipic, caproic, and oxalic acids)	Lab scale	(EED) membrane effective area 81 cm ² ; voltage drop: 5–15 V; current efficiency: 20.86–42.14%	EC: 3.92–22.84 kWh/kg acids recovered	[34]

Table 3 (Continued)

Application	Scale	ED process characteristics	Economic estimation	References
Recovery of pyruvate	Lab scale	(CED) membrane effective area: 36 cm ² ; current density: 3.97 mA cm ⁻² ; current efficiency: 93.3%; initial pyruvate concentration: 50 g L ⁻¹ ; pyruvate flux: 367 g m ⁻² h ⁻¹ ; pyruvate recovery: 94.9%	EC: 1.4 kWh/kg of pyruvate	[28]
Production of L-malic acid	Lab scale	(EED) membrane effective area 100 cm ² ; current density: 0.5–2.5 mA cm ⁻²	No information available	[35]
Production of Vitamin-C (ascorbic acid)	Lab scale and semi-industrial pilot	(Two-compartment EDBM) current density: 1000 A/m ² ; current efficiency: 75%; acid concentration: 1 M	EC: 1.4–2.3 kWh/kg acid	[41]
Production of gluconic acid and Vitamin C	Lab scale	(Two-compartment EDBM) membrane effective area 98 cm ² ; current efficiency: 70% (average); conversion ratio: 98%	EC: about 1 kWh/kg of acid	[50]
Production of salicylic acid	Lab pilot	(Three-compartment EDBM) Tokuyama BM; elementary cell voltage: 30 V at 750 A/m ² ; current efficiency: 80–90% at 40 °C; acid concentration: 4.5 (maximum) g L ⁻¹	EC: 15–20 kWh/kg of product	[48]
Production of salicylic acid (HSa)	Lab scale	(TPEIS) membrane area (cm ²): 41; initial composition: 0.5 mol L ⁻¹ NaSa in a water–ethanol (1:1) solution; yield (mol): 0.067 (300 A/m ² , 3 h); conversion rate of NaSa into HSa (%): 96%	No information available	[52]
Recovery of methanesulphonic acid (MTA)	Industrial plant	(Three-compartment EDBM) membrane area: 64 m ² ; elementary cell voltage: 2.26 V at 800 A/m ² ; methanesulphonic conversion ratio: 95%; concentration: MTS 250, MTA 100, NaOH 80 g L ⁻¹	No information available	[41]
Regeneration of camphorsulphonic acid	Pilot-scale	(Three-compartment EDBM) BM area: 0.14 m ² ; current density: 500 A/m ² ; Faradic yield: 7%; salt conversion: 98.5%; final acid concentration: 0.8 M	EC: 3 kWh/kg of acid	[41]
Regeneration of <i>p</i> -toluenesulfonic acid	Lab scale	(Two-compartment EDBM) mean current efficiency: 50%	EC: 1.2 kWh/kg acid	[47]

EC: energy consumption.

5.2. Sensitivity analysis

In fact, it is very difficult to do an accurate economic analysis on ED processes because it varies with external factors (location, production capacity, individual application, membrane price, etc.) and internal ones (membrane properties, feed conditions, product quality requirements, operation parameters, etc.). However, if one wants to conduct a preliminary assessment on the process, it is better to take an extra effort to do a sensitivity analysis. The analysis is not only beneficial to the reliability of the process cost, but also useful for the improvement on cost management. Naturally, sensitivity analyses are different from case to case, but there are some common factors necessary for the analysis on ED processes, i.e., running chemicals' cost, electricity charge, membrane cost, and peripheral equipment cost. As for the detailed procedures for the analysis, the literature [32] can be referred to.

6. Challenges and perspective

As discussed above, ED has shown its competence in the production of organic acids. However, more improvements are needed for adapting ED to industrialization, and more research needs to be conducted for optimizing operation parameters and

process integration. The goals include (1) decreasing membrane cost, especially the cost of bipolar membranes, (2) improving the anti-fouling properties of membranes, and (3) increasing the selectivity for co-ions and developing ion-exchange membranes with a specific selectivity for organic anions or hydrogen ions.

Notably, membrane fouling is the most significant hurdle for the industrialization of membrane techniques and should be considered throughout the operation process. Apart from the pretreatments mentioned above, more measures should be taken to eliminate or abate membrane fouling while the ED stack is working and after it is shut down. The measures include (1) periodically reversing the polarity of electrodes (EDR, electrodialysis reversal), (2) decreasing operating current, (3) improving the hydraulic conditions in stack compartments by increasing feed rate or employing gaskets with flow paths [61], (4) adding chemicals to suppress the formation of precipitates and the propagation of microbes, (5) extracting products before saturation, (6) using membranes with tailored properties, such as mono-valent membranes [62], and (7) hydraulically, mechanically and/or chemically cleansing membranes after the stack is shut down. It is expected that improvements can be achieved on these measures and contribute to enhancing and prolonging ED operation without deteriorating the product quality or increasing energy consumption or chemicals' cost significantly.

The ideal module for applying ED to organic acid production is a reactor or bioreactor integrated with ED, which can realize in situ separation, purification, and production adjustment without any apparent retrogression in its function (for example, membrane fouling or erosion, leakage, etc.). To bring that ideal to realization, the academia, industry, and government should gather together to make a concerted effort. We hope that, apart from the separation and conversion of organic acids or organic salts, ED can promote the comprehensive utilization of renewable resources and contribute to the sustainable development of humankind.

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