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Simultaneous regeneration of formic acid and carbonic acid from oxalate discharge by using electrodialysis with bipolar membranes (EDBM)

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Abstract

The feasibility was tested on simultaneous generation of formic acid and carbonic acid from oxalate discharge by using two-compartment electrodialysis with bipolar and anion exchange membranes. The process performances were evaluated by considering such factors as the molar ratio of sodium formate to sodium carbonate, and current density. The results indicated that current efficiency could attain 72% and 21% for the generation of formic acid and carbonic acid, respectively. The energy consumption was 4.3–16.6 kWh kg^{-1} for formic acid and 20.1–96.3 kWh kg^{-1} for carbonic acid. When the molar ratio of sodium formate to sodium carbonate was in the range of 0.5–2, formate anions would be the main current carriers through the anion exchange membrane, and the molar concentration of formic acid could achieve 12 times that of carbonic acid in the product solution. This can be mainly ascribed to the high permselectivity of the anion exchange membrane for formate anions. Notably, a third competitive species – OH^- – is not negligible in the acid reclaiming system by using EDBM.

Keywords: Formic acid; Carbonic acid; Electrodialysis; Bipolar membrane; Oxalate discharge

1. Introduction

Oxalic acid is a carboxylic acid which has been widely used in dairy, medicine and other chemical industries [1]. Its preparation methods include synthesis from sodium formate, and oxidation of carbohydrate, glycol, or propane [2]. In China, the first method mentioned above is mainly adopted to produce oxalic acid, which follows the procedures as thermal dehydrogenation, water cooling, and acidification (Fig. 1). Sodium oxalate is separated during water cooling, so the residual liquor contains two main ingredients: (1) unreacted sodium formate, and (2) sodium carbonate, which is formed in the following side reaction:

- Dehydrogenation: $2HCOONa = Na_2C_2O_4 + H_2\uparrow$
- Side reaction: $2HCOONa = Na_2CO_3 + CO\uparrow + H_2\uparrow$

Typically, the molar ratio of sodium formate to sodium carbonate is up to 2:1 (0.8:0.4 mol dm^{-3} [3]). Such liquor contains valuable materials but has been polluting the environment since it is often discharged without further treatment.

Electrodialysis with bipolar membranes (EDBM) has peculiar functions because it integrates the water splitting of bipolar membranes and the salt dissociation of conventional electrodialysis. Since this technology has been widely used for resource recycling and/or pollution treatment while production is undergoing, EDBM is considered a sustainable technology [4,5], especially, a versatile tool for organic acid production or recovery from the corresponding salts with maximum alleviation or elimination of pollution [6–8].

Till now, EDBM has been used to acid and/or base production or regeneration, acidification or alkalization, and organic syntheses, which have been summarized in our recent review [9]. Although abundant examples have proved the feasibility of such technology, in most cases, its application is limited to the pure organic acid system, *i.e.*, few worked on the simultaneous production of two acids. In this paper, the feasibility of simultaneous recovery of acid mixture will be tested by using model oxalate discharge. Fig. 2 illustrates the principle of generating acids from model oxalate discharge. Anion exchange membranes and bipolar membranes are positioned alternatively to form salt/base

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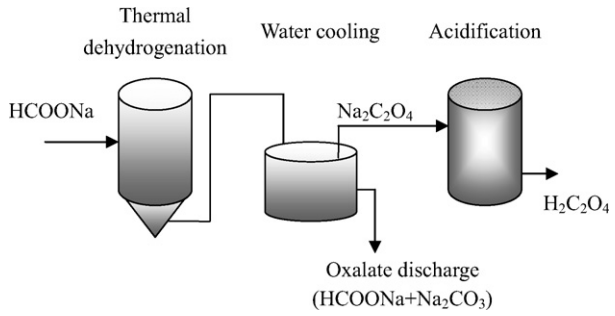

Fig. 1. Schematic of a conventional process to synthesize oxalic acid from sodium formate.

compartment and acid compartment. When a direct current is passed through the membrane stack, $HCOO^-$ and CO_3^{2-} transport through the anion exchange membrane and form HCOOH and H_2CO_3 in the acid compartment by association with protons provided by the bipolar membrane [10]. Meanwhile, in the salt/base compartment, the hydroxyl ions (generated by the other bipolar membrane) combine with sodium ions to form sodium hydroxide.

Obviously, Fig. 2 presents an EDBM stack of BP-A configuration (BP, bipolar membrane; A, anion exchange membrane), which is not the conventional configuration used for production of a single acid by using EDBM:BP-C configuration (C, cation exchange membrane). There are some reasons why BP-A configuration is chosen for experiments. For one thing, BP-C configuration is not desirable for impurity removal since it keeps the feed and product in the same compartment. For another, BP-A configuration makes it possible to investigate the competition between acid anions (not possible in BP-C configuration) and the advantage and disadvantage of OH^- migration (accelerating the dissociation of acid molecules; competing with acid anions as current carriers). BP-C–A configuration can meet the same purpose but the stack of this configuration has larger electrical resistance than that of BP-A configuration. Correspondingly, an EDBM stack of BP-A configuration is chosen for a preliminary research on a comparatively complex subject—simultaneous generation of two acids by using EDBM. In this paper, the factors affecting the process, such as the molar ratio of sodium formate to sodium carbonate, and current density, will be investigated, and the competition between formate and carbonate anions will be clarified.

2. Experiment

2.1. Materials

The membranes used for experiments were FT-FAB and Neosepta BP-1, and their properties are listed in Table 1. All the chemicals were of analytical grade.

2.2. Set-up

The laboratory-scale experimental set-up was composed of a bipolar membrane and an anion exchange membrane between two electrodes [11], and the three compartments formed were salt/base compartment, acid compartment and anode compartment. Each compartment was connected to a separate external 500 cm^3 beaker, allowing for continuous circulation by three immersible pumps (AP1000, Zhongshan Zhenghua Electronics Co. Ltd., China). The effective membrane area was 7.07 cm^2. The electrodes were made of titanium coated with ruthenium. Model oxalate discharge (containing HCOONa and Na_2CO_3) was added into salt/base compartment. Na_2SO_4 was added in acid compartment and anode compartment to reduce electrical resistance as electrolyte and its concentration was 0.35 mol dm^{-3}. The volume was 500 cm^3 for each of the two compartments. All the experiment runs were kept at the equal temperature $T = 298$ K. The molar ratio of HCOONa to Na_2CO_3 was 0.8:0.4, 0.4:0.4, or 0.4:0.8. Current density was 20, 50, or 80 mA cm^{-2}.

2.3. Determination of acid concentration

The concentration of total acid (equiv. dm^{-3}) was determined by titration with standard sodium hydroxide solution using phenolphthalein (pH 8–9.8) as indicator. The concentration of formic acid was determined by titration with standard sodium hydroxide solution using methyl orange (pH 3.1–4.4) as

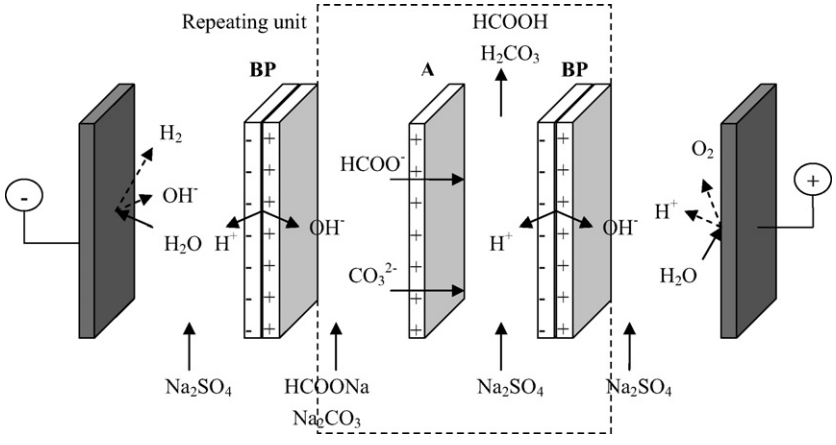

Fig. 2. Principle of treating model oxalate discharge by using EDBM: A, anion exchange membrane; BP, bipolar membrane.