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Modeling of a packed-bed electrochemical reactor for producing glyoxylic acid from oxalic acid

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Abstract

A two-dimensional reactor model was established for a packed-bed electrochemical reactor with cooled cathode (PERCC) for producing glyoxylic acid from oxalic acid based on the system's reaction kinetics, mass conservation equation, and the equation of charge conservation in terms of solution-cathode potential to describe the distributions of glyoxylic acid concentration and electrolyte potential in the cathode compartment of the PERCC. The equation for a circulating mixer was also presented to account for the accumulation of glyoxylic acid in the catholyte of a batch electroreduction process. Using the orthogonal collocation approach, the partial differential equations of the model could be converted into sets of algebraic equations and be numerically solved. The effects of operating temperature, conductivity of catholyte, operating cathode potential, and volumetric flow rate of the catholyte on the current efficiency and concentration of glyoxylic acid were simulated and discussed, with emphasis on the current densities generated from main and side reactions. The model was used in a batch operation process and a continuous operation process, with the predicted results being generally in good agreement with the experimental data for both the cases.

Keywords: Glyoxylic acid; Packed bed; Electrochemical reactor; Cooled cathode; Mathematical modeling; Continuous operation

1. Introduction

Glyoxylic acid, the simplest aldehyde acid, is extensively utilized in many fine chemical industries such as perfumery, pharmaceutical, cosmetic, etc. Various reduction or oxidation methods in industrial production of glyoxylic acid have received great attention by many researchers. Among those methods, the electrochemical reduction of oxalic acid to produce glyoxylic acid has been suggested as one of the most acceptable technologies because it meets the increasing and stringent requirements for environmental protection following the rapid development of world economy. It has also many other advantages, such as less investment for the processing plants, low cost of the raw material, and easy separation of the product.

Although the production of glyoxylic acid by the electrochemical reduction of oxalic acid has been commercialized for many years, there are still two major problems which remain incompletely solved: the cathode material (lead) can be easily deactivated due to the presence of metals with low hydrogen overvoltage (Scott, 1986); in addition, the traditional parallel electrode reactor (PER) has usually a low space–time yield (STY). With respect to the former problem, many improvements were proposed either by chemical cleaning (Goodridge et al., 1980) or by use of chemical additives (activators) (Ochoa et al., 1993; Zhou et al., 2003); also it is possible to find some replaceable cathode materials such as platinum-based Pb–Sb catalysts investigated by Xia et al. (2001). For the latter case, we explored the packed-bed electrochemical reactor with cooled cathode (PERCC) (Fan et al., 2004) in an engineering sense based on the concept suggested by Scott (1992) with the purpose to improve the STY of the traditional electrochemical reactors such as PER.

Removal of the reaction heat to maintain a constant operating temperature is a key factor for the reduction of oxalic acid in a packed-bed electrochemical reactor. The PERCC is a three-dimensional (3-D) electrochemical reactor installed with cathode packings between series of cathode tubes that act either as heat exchangers or reaction surfaces. For a simple case, Fig. 1 shows a batch operation experiment using PERCC

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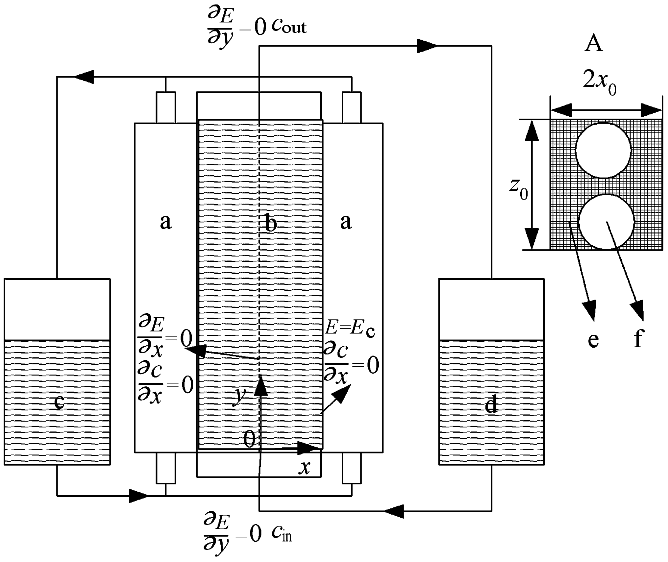

Fig. 1. Schematic diagram of a batch electroreduction process and the PERCC reactor. (A) Cross-section of the PERCC; (a) anode chamber; (b) cathode chamber; (c) anolyte; (d) catholyte (in a circulating mixer); (e) cathode packings; (f) tube cathodes (cooling medium inside).

(Fan et al., 2004).The PERCC was composed of a cathode chamber between two anode chambers, and installed with two cathode tubes in the cathode chamber. Packings were filled into the space between the tubes, with the material of both tubes and packings being made of lead with a purity of 99.99%. The reaction temperature (±0.2 K) could be controlled by adjusting the flow rate and temperature of the coolant ethanol inside the cathode tubes. In the experiment, the catholyte and anolyte were saturated oxalic acid and 20% (in mass) sulfuric acid aqueous solutions, respectively, which were separated by an ion-exchange membrane (CM001) purchased from Shanghai Qiujiang Factory, China, and circulated by two magnetically driven pumps. Before the experiment, the volumetric flow rate of the electrolyte was calibrated by using a stopwatch and graduated cylinders. A PerkinElmer Lambda 35 UV/Vis Spectrometer was used to determine the glyoxylic acid concentration in catholyte at the wavelength of 220 nm.The Cannizzaro reaction (Scott, 1991) was used to detect glyoxal produced from the electroreduction of glyoxylic acid. Cathode potential (±0.01 V), the voltage between a cathode feeder and a saturated calomel electrode (sce), was measured by a digital Ohmmeter and controlled by tuning a power supply provided by Xiamen Rectifier Factory, China. The cathode feeder was connected to the cathode tubes, and the sce was connected with a luggin capillary close to the boundary ($x = x_0$) where the ion-exchange membranes were installed. Saturated oxalic acid solution of the catholyte was guaranteed by adding excess oxalic acid in the circulating mixer throughout the experiment.

Because the PERCC has a relatively large specific area, it is possible to achieve a high STY for electroreduction of oxalic acid, and carry out a continuous operation mode feeding the saturated oxalic acid solution at one side of the reactor and producing glyoxylic acid with the desired concentration at the other side of the reactor. In comparison with the two-dimensional (2-D) PER, the distributions of current, potential, temperature and concentration within the 3-D reactor are more complicated. Meanwhile, the geometry of electrodes, conductivity of electrolytes and electrodes, and hydrodynamics of electrolytes in a 3-D reactor may also obviously influence the distributions of the variables mentioned above. Consequently, theoretical surveys of the reactor in detail are necessary for an optimum operation and a further scale-up of the process.

This work is aimed at the modeling of the PERCC, and introduces its applications to both a batch operation process and a continuous operation process for electroreduction of oxalic acid to glyoxylic acid.

2. Reactor model

Fundamentals and applications of the packed-bed electrochemical reactor were intensively studied in the past (Newman and Tobias, 1962; Alkire and Ng, 1977; Storck et al., 1982, Xu et al., 1992, Zhang et al., 1999). Indeed, a mathematical model of a reactor should be capable of describing the distributions of product or reactant concentrations in the reactor, electrolyte temperature and electrolyte potential. The fundamental equations of a model should therefore include: (1) reaction kinetics; (2) equation of conservation of charge; (3) equation of conservation of mass; and (4) equation of conservation of energy. Because we are interested in glyoxylic acid only and the cathode chamber is separated from the anode chamber by an ion-exchange membrane for the investigated reactor, the model will be established for the cathodic region only. Since the reaction heat from the reduction of oxalic acid in the cathode chamber can be removed quickly due to the cooled cathodes employed (Fan et al., 2004), the equation of conservation of energy is avoided for an isothermal operation. To simplify the mathematical treatment, further assumptions are required: (1) both the fixed solid phase (cathode) and the liquid phase (catholyte) are continuous; (2) it is a steady plug flow in the reactor for the continuous operation process and also for the batch operation process in a period of differential time; and (3) a flow-by operation mode considering the catholyte flow direction y and the current direction x, as shown in Fig. 1, is adopted because the depth is relatively small compared with the length of the reactor.

2.1. Reaction kinetics

The main reaction on the cathode surface is the reduction of oxalic acid into glyoxylic acid:

$$\mathrm{COOHCOOH} + 2\mathrm{H}^+ + 2\mathrm{e}^- \xrightarrow{i_1} \mathrm{COOHCHO} + \mathrm{H_2O}. \qquad (1)$$

The side reactions involve further reduction of glyoxylic acid into glycollic acid or glyoxal and the generation of hydrogen:

$$\mathrm{COOHCHO} + 2\mathrm{H}^+ + 2\mathrm{e}^- \xrightarrow{i_2} \mathrm{COOHCH_2OH}, \qquad (2)$$

$$2\mathrm{H}^+ + 2\mathrm{e}^- \xrightarrow{i_3} \mathrm{H_2}, \qquad (3)$$

$$\mathrm{COOHCHO} + 2\mathrm{H}^+ + 2\mathrm{e}^- \xrightarrow{i_4} \mathrm{CHOCHO} + \mathrm{H_2O}. \qquad (4)$$