Integration of anodic and cathodic processes for the synergistic electrochemical production of peracetic acid

I. Moraleda, J. Llanos *, C. Sáez, M.A. Rodrigo, P. Cañizares

Chemical Engineering Department, Facultad de Ciencias y Tecnologías Químicas, University of Castilla-La Mancha, Edificio Enrique Costa Novella, Av. Camilo José Cela n° 12, 13071 Ciudad Real, Spain

ARTICLE INFO

ABSTRACT

Efficient in-situ production of peracetic acid is an unreached milestone of electrochemical engineering. Previous attempts in the production of peracetic acid were focused either on the cathodic production of hydrogen peroxide and its further addition to acetic acid solutions or on the oxidation of a suitable raw material (v. g. acetic acid, acetaldehyde, ethanol). In the present work, the oxidation of acetic acid by a boron doped diamond (BDD) anode was integrated with the cathodic production of hydrogen peroxide using a carbon felt gas diffusion electrode. A marked synergistic effect (synergy coefficient of $192.0 \pm 13.1\%$) is observed when the oxidation of acetic acid by hydroxyl radicals is performed together with the cathodic production of hydrogen peroxide. A maximum PAA production efficiency of 19.87% was obtained, a value much higher than previous works based on the oxidation of acetic acid by BDD anodes and approximately double the optimal value reported in studies based on the production of hydrogen peroxide.

1. Introduction

Organic peroxyacids are characterized by the substitution of their hydroxyl group (—OH) by a peroxide group (—O—OH). Among them, peroxyacetic acid (also referred to as peracetic acid) (PAA), is proposed to be used in a wide range of applications, such as disinfectant [1–3], sludge treatment [4], removal of organic pollutants [5], organic synthesis processes [6] and bleaching agent [7]. PAA is commercially available as a mixture with acetic acid and hydrogen peroxide and one of the reaction pathways for the production of PAA is the oxidation of acetic acid by hydrogen peroxide [8] (Eq. (1)).

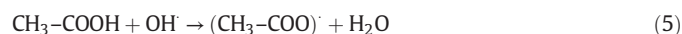$$CH_3COOH + H_2O_2 \leftrightarrows CH_3COOOH + H_2O \tag{1}$$

As with many other oxidants, the in-situ production of PAA is worth investigating in order to limit the costs and hazards related to the transport and handling of concentrated PAA [9]. Some approaches to the in-situ production of PAA are based on the equilibrium represented by Eq. (1). Thus, Saha et al. studied the synthesis of PAA by the addition of electrochemically produced hydrogen peroxide (Eq. (2)) to a solution of acetic acid [10]. In this work, Saha et al. used a gas diffusion electrode (GDE) doped with Pt as cathode, in order to promote the formation of oxygen radicals, which can also produce PAA following the reaction represented by Eq. (3). In this work, current efficiencies in the production of PAA from 1 to 10% were achieved.

$$H^+ + \tfrac{1}{2} O_2 + 2 e^- \leftrightarrows H_2O_2 \tag{2}$$

$$CH_3COOH + O^. \rightarrow CH_3COOOH \tag{3}$$

A different approach was proposed by Cotillas et al., who performed the electrochemical oxidation of different raw materials (ethanol, acetaldehyde and sodium acetate) by boron doped diamond anodes (BDD) [11]. In this case, the oxidation process is based on the production of hydroxyl radicals (Eq. (4)), which can oxidize the raw materials to form the desired PAA (Eqs. (5) and (6)) for the oxidation of acetic acid). In this case, the main drawbacks reported were the low current efficiencies and the high degree of mineralization of the raw materials employed. A few other attempts in the design of efficient electrochemical production of different chemicals by combining anodic and cathodic reactions have also been published [12–14], but none of them have been focused on the production of PAA.

$$H_2O \rightarrow OH^. + H^+ + e^- \tag{4}$$

$$CH_3-COOH + OH^. \rightarrow (CH_3-COO)^. + H_2O \tag{5}$$

$$(CH_3-COO)^. + OH^. \rightarrow CH_3-COOOH \tag{6}$$

In the present work, a novel approach for the efficient production of PAA from acetic acid solutions is presented for the first time. The

* Corresponding author.
E-mail address: javier.llanos@uclm.es (J. Llanos).

prototype proposed combines the cathodic production of hydrogen peroxide together with the anodic oxidation of acetic acid. This cell is composed of a carbon felt cathode, which acts as gas diffusion layer, and a BDD anode and, as it is going to be explained, it is expected to exhibit a marked synergistic effect in the yield and efficiency of PAA production, as compared to the single processes.

2. Experimental

2.1. Experimental set-up

The cell proposed in the present work is schematized in Fig. 1. It consists of a carbon felt (CF) cathode, which acts as a gas diffusion electrode (GDE) and separates the gas phase from the cathodic chamber, and a BDD anode, on which the oxidation of acetic acid is performed. A cationic exchange membrane (NAFION N-117) is placed to separate both compartments. The feed solution (10% aqueous acetic acid) enters the reactor through the anodic chamber (where the oxidation of acetic acid is expected) and is then circulated through the cathodic compartment, where the production of hydrogen peroxide is expected to occur. The volumetric flow rate of the solution was 15.37 L h^{-1}. Non-aerated experiments were performed by removing the gas chamber from the reactor.

The BDD anode is a rectangular piece with a geometric area of 1824 mm^2. Boron-doped diamond (BDD) films were provided by Adamant (Switzerland) (currently NeoCoat, France) and synthesized via the hot-filament chemical vapor deposition (HF CVD) technique on single-crystal p-type Si (100) wafers (0.1Ω cm, Siltronix). The BDD had a thickness of 2.7 μm, a boron concentration of 500 ppm and a sp^3/sp^2 ratio of 258. Dimensional Stable Anode (DSA®, DeNora, Italy) was a rectangular mesh with a geometric area of 1890 mm^2, with a short and long way of mesh of 3 and 8 mm and a strand width of 1 mm. Carbon felt (SGL Carbon, Spain) is used as cathode. CF is rectangular with a geometric area of 3375 mm^2. It is synthesized following a procedure described elsewhere [15,16], which consists of immersing a CF piece into an ink in an ultrasonic bath. This ink is composed of 30 mL distilled water, 0.3 g carbon black (Vulcan ® XC72R), 0.3 g PTFE (60% Teflon ® emulsion solution from ElectroChem, Inc.) and 3% n-butanol.

The solution is stored in an amber glass tank and was recirculated towards electrolytic cell by means of a centrifugal pump. The temperature was kept constant at 25 °C by a heat exchanger. The intensity applied to all tests was 0.05 A, the electrolysis time was 18 h and the reactor volume was 0.4 L.

2.2. Analytical procedures

The determination of PAA was performed by two different methods. The first was based on the selective oxidation of 2,2'-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) by PAA in the presence of potassium iodide [17]. 20 μL of the sample were mixed with 2 mL of acetic acid (1 M), 1 mL of ABTS solution (1 mg/mL) and distilled water to reach a total volume of 10 mL. The absorbance was determined at 732 nm by means of an Agilent 300 Cary series UV–Vis spectrophotometer.

The second method was based on an indirect determination of PAA by subtracting the concentration of hydrogen peroxide from the total concentration of oxidants. The total oxidants were determined by titration with $Na_2S_2O_3$, following this procedure: 5 mL of 20% (v/v) H_2SO_4 solution were added to 10 mL of sample with an excess of solid KI. The iodide was oxidized to form brownish iodine, which was titrated with 0.002 N $Na_2S_2O_3$ until a colorless solution. Hydrogen peroxide was determined by potassium titanium (IV) using the oxalate method [18]. Sigma-Aldrich supplied all reagents used and the titanium solution was supplied by Fluka. The absorbance was determined at 410 nm by an Agilent 300 Cary series UV–Vis spectrophotometer. It was checked that both methods predict similar concentrations of PAA.

3. Results and discussion

Three configurations were tested in order to evaluate the role of both cathodic and anodic reactions in the synthesis of PAA: 1) BDD as anode and aeration on the cathode GDE (BDD-air); 2) DSA® as anode and aerated cathode (DSA-air); 3) BDD as anode and non-aerated cathode (BDD-no air). The three configurations used carbon felt as cathode and all tests were performed in triplicate. Fig. 2 represents the amount of PAA and H_2O_2 generated, including standard deviation as error bars.

As it is observed, the system BDD-air clearly overcomes the performance of the device equipped with DSA and the system without aeration. The marked difference in the performance of the systems with and without aeration is explained on the basis of the role of H_2O_2 in the production of PAA. In a reaction media with a high concentration of acetic acid and with no presence of H_2O_2, the chemical equilibrium
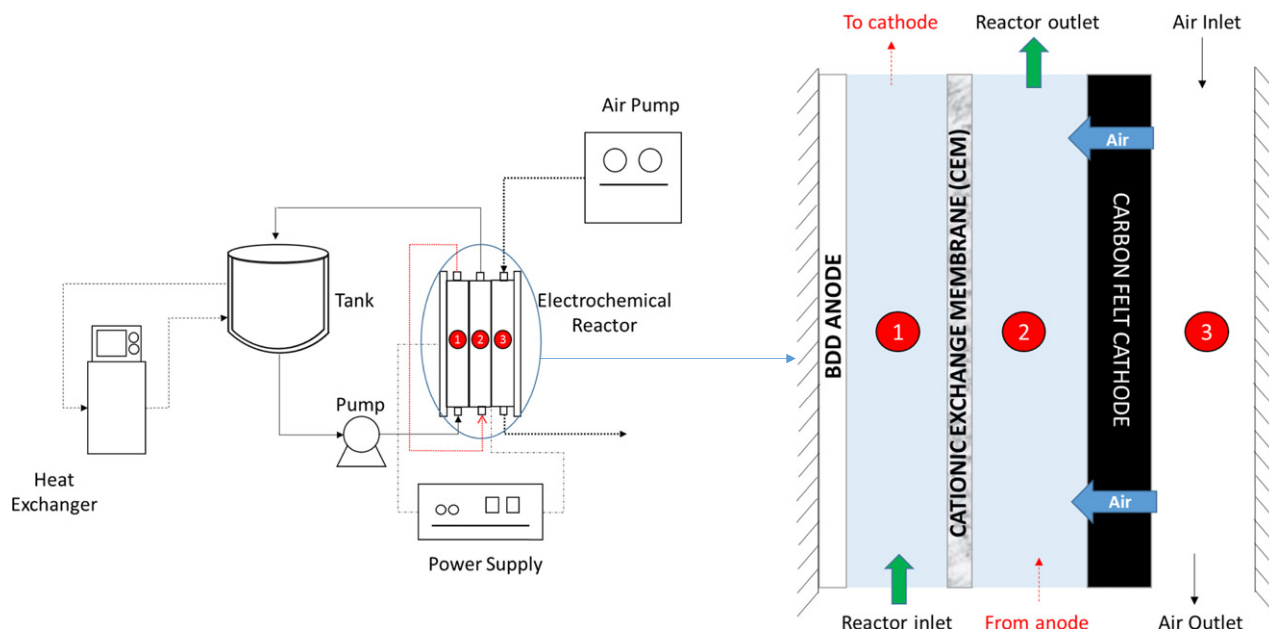

Fig. 1. Scheme of electrochemical cell used to synthesis of PAA and hydrogen peroxide. 1) Anodic chamber; 2) cathodic chamber; 3) gas chamber.