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

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Abstract

Efficient in-situ production of peracetic acid is an unreached milestone of electrochemical engineering. Previous attempts to 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±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 than the optimal value reported in studies based on the production of hydrogen peroxide.

Keywords: peracetic acid; gas diffusion electrode; hydrogen peroxide; BDD; carbon felt

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] (Equation 1).

$$CH_3COOH + H_2O_2 \leftrightarrows CH_3COOOH + H_2O \quad (1)$$

As with many other oxidants, the in-situ production of PAA is worth to be investigated 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 Equation 1. Thus, Saha et al. studied the synthesis of PAA by the addition of electrochemically-produced hydrogen peroxide (Equation 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 Equation 3. In this work, current efficiencies in the production of PAA from 1 to 10 % were achieved.

$$H^+ + \tfrac{1}{2} O_2 + 2\, e^- \leftrightarrows H_2O_2 \quad (2)$$

$$CH_3COOH + O^{\cdot} \rightarrow CH_3COOOH \quad (3)$$

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 (Equation 4), which can oxidize the raw materials to form the desired PAA (equations 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.

$H_2O \rightarrow OH^{\cdot} + H^+ + e^-$ (4)

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

$(CH_3\text{-}COO)^{\cdot} + OH^{\cdot} \rightarrow CH_3\text{-}COOOH$ (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 prototype proposed combines the cathodic production of hydrogen peroxide together with the anodic oxidation of acetic acid. This cell is composed by 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 Figure 1. It consists in 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.

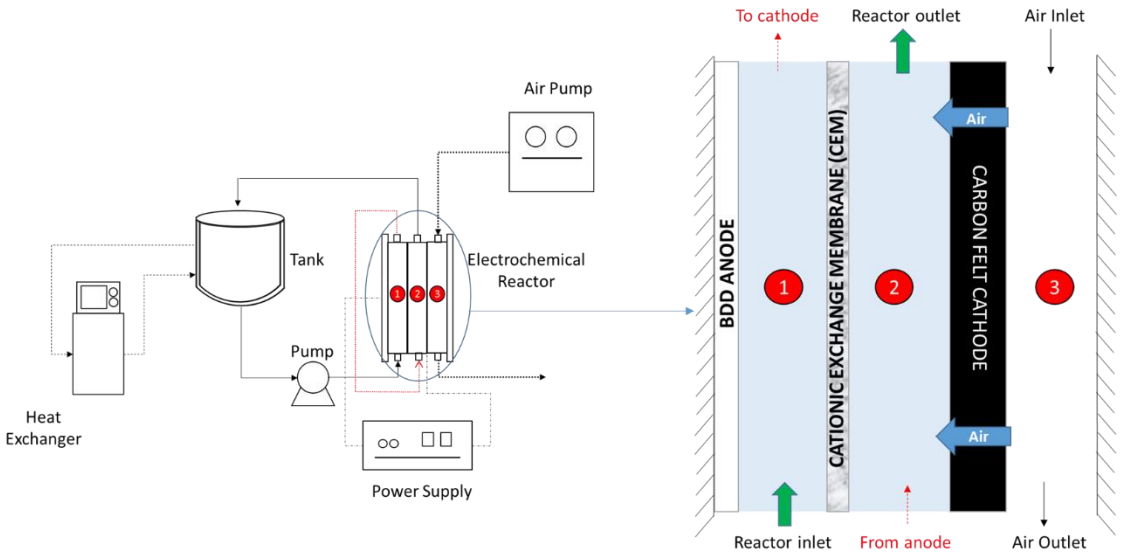

Figure 1: Scheme of electrochemical cell used to synthesis of PAA and hydrogen peroxide. 1) anodic chamber; 2) cathodic chamber; 3) gas chamber

The BDD anode is 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 (0.1 Ω 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 [12, 13], which consist in immersing a CF piece into an ink in an ultrasonic bath. This ink is composed by 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 amber glass tank and was recirculated towards electrolytic cell by means of a centrifugal pump. The temperature was kept constant at 25ºC by a heat exchanger. The intensity applied to all tests was 0.1 A 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 [14]. 20 µL of the sample are mixed with 2 mL of acetic acid (1M), 1 mL of ABTS solution (1mg/mL) and distillated water to reach a total volume of 10 mL. Sigma-Aldrich supplies all reagents used. The absorbance is determined at 732 nm by means of an Agilent 300 Cary series UV-Vis spectrophotometer.

The second method is based in 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 is oxidized to form brownish iodine, which is titrated with 0.002 N $Na_2S_2O_3$ until a colorless solution. Hydrogen peroxide is determined by potassium titanium (IV) using oxalate method [15]. The titanium solution is supplied by Fluka and the absorbance is 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. Figure 2 represents the amount of PAA and H_2O_2 generated, including standard deviation as error bars.

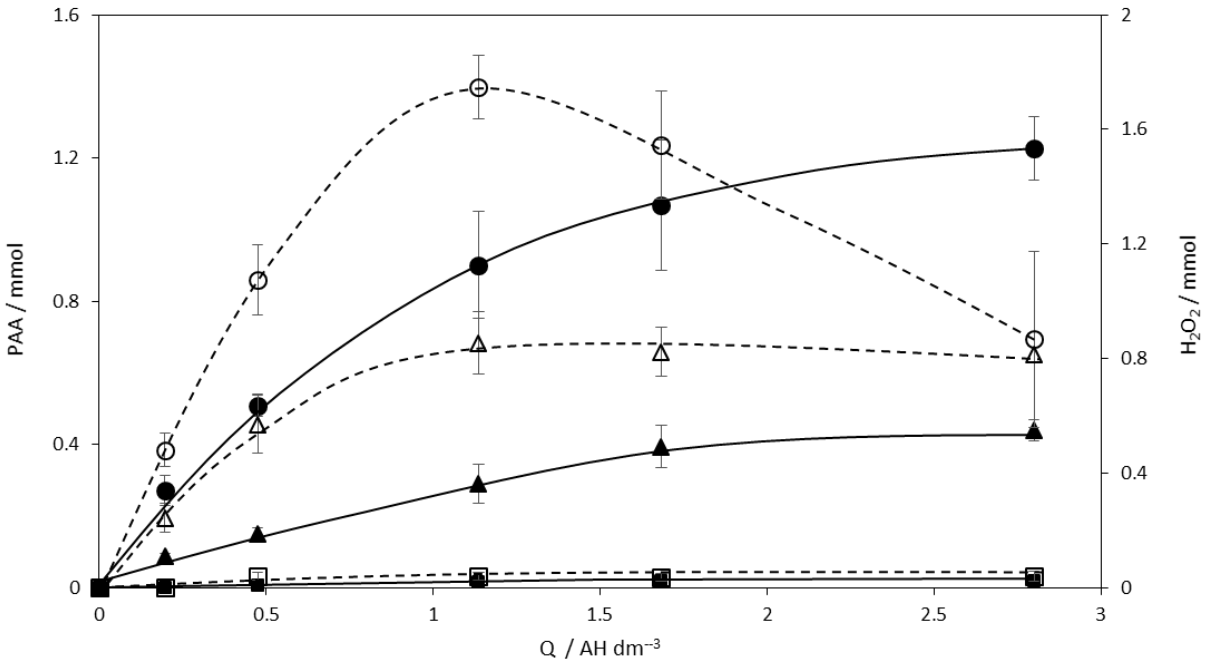

Fig. 2. Evolution of the amount of PAA (full symbols) and hydrogen peroxide (empty symbols) with applied electric charge. ●, ○ BDD-air; ▲,△DSA-air; □, ■ BDD-no air.

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 described by Eq. 1 is easily shifted to the left, causing the consumption of peracetic acid. As H_2O_2 produced is expected to be negligible in the system without aeration, the maximum amount of PAA produced in the BDD-no air device (0.02 mmol) is two orders of magnitude lower than that obtained in the system with BDD anode and aeration (1.24 mmol).

In order to quantify the improvement of BDD-air system regarding PAA production, a synergy coefficient (S_{PAA}, %) was defined according to Equation 7, being $PAA_{BDD\text{-}air}$, $PAA_{DSA\text{-}air}$ and $PAA_{BDD\text{-}no\ air}$ the amount of PAA (mol) produced in the three systems tested. This parameter was calculated for the different applied electric charges, reaching a nearly constant value of 192.0±13.1% throughout the tests.

$$S_{PAA} = \frac{PAA_{BDD-air} - PAA_{DSA-air} - PAA_{BDD-no\ air}}{PAA_{DSA-air} + PAA_{BDD-no\ air}} \cdot 100 \qquad (7)$$

As commented in the introduction section, PAA can be produced either by hydroxylation of acetic acid by hydroxyl radicals (equations 5 and 6) and/or by the reaction between acetic acid and hydrogen peroxide (Equation 2). In the BDD-air system, the anodic material facilitates the production of hydroxyl radicals [16], enhancing the production of PAA by hydroxylation of acetic acid together with its reaction with the hydrogen peroxide produced at the cathode. Unlike in the case of BDD-air system, the amount of hydroxyl radicals is expected to be negligible in the case of working with the DSA® anode. Thus, PAA is produced only through the reaction of acetic acid and H_2O_2 in the case of the DSA-air reactor.

Moreover, according to the data gathered in Figure 2, a higher concentration of H_2O_2 is also detected in the reactor BDD-air, compared to the system DSA-air. This higher concentration of H_2O_2 is explained by a partial decomposition of PAA according to Equation 1 and by the recombination of hydroxyl radicals, Equation 8 [17, 18]. The greater decomposition rate of H_2O_2 due to the higher concentration [19, 20] elucidates the decrease in hydrogen peroxide observed at the two highest values of electric charge of the BDD-air system.

At this point, it is possible to compare the performance of both aerated systems by dividing the amount of a compound (PAA or H_2O_2) produced in the BDD-air cell by that obtained in the DSA-air device at the same value of applied electric charge. These ratios were calculated for the different applied electric charges, giving values of 3.02±0.12 and 1.77±0.18 for PAA and H_2O_2, respectively. This means that the enhancement in the production of PAA in the BDD-air device is higher than the increase in the accumulation of H_2O_2, supporting that the improvement in PAA production of the BDD-air cell is not only due to the higher H_2O_2 detected but also due to the key role of the hydroxyl radicals produced by the BDD anode.

$$2\ OH^{\cdot} \rightarrow H_2O_2 \qquad (8)$$

Finally, Fig. 3 represents the evolution of the current efficiency in the production of PAA with respect to the applied electric charge. As expected, the maximum efficiency was obtained at the lowest applied electric charge and was equal to 19.87%. This value is much higher than previous works of PAA synthesis by BDD oxidation [11] and approximately double than the maximum value reported with a reactor based on the cathodic formation of H_2O_2 [10]. At this point, it is worth mentioning that in that work,

the reactor was fed by pure oxygen, being the production of hydrogen peroxide more efficient than in the present work (reactor fed by air). Hence, the configuration studied in this work is particularly promising for the synthesis of PAA and further work is being done currently for its development.

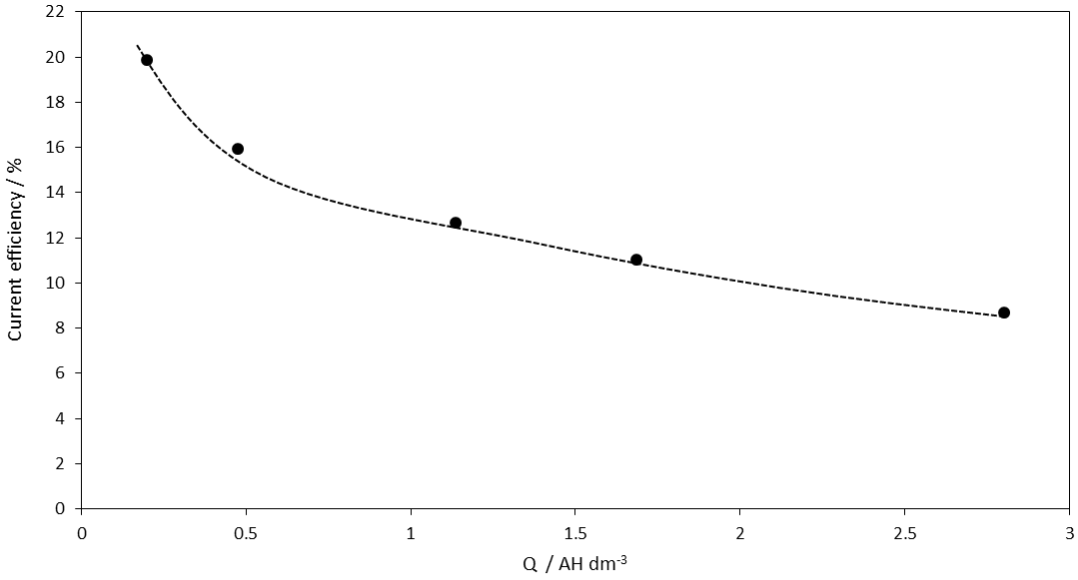

Fig. 3. Current efficiency for the production of PAA with respect to the applied electric charge.

4. Conclusion

In the present work, a novel electrochemical cell based on a BDD anode and a carbon felt cathode is developed for the production of PAA from acetic acid. The integration of the production of hydroxyl radicals at the anode and the formation of hydrogen peroxide at the cathode is demonstrated to be clearly synergistic with respect to the single production mechanisms of PAA. A maximum PAA production efficiency of 19.87% was obtained, a value clearly above previous studies on the production of PAA by electrochemical methods.

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