



The jet aerator as oxygen supplier for the electrochemical generation of H₂O₂



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ABSTRACT

The hydrogen peroxide is a key and versatile compound that can be readily produced in one-pot electrochemical reactors via the 2 e⁻ oxygen reduction reaction. In all the electrolyzers studied up to date, the external aeration is carried out by means of a compressor. In this work, the compressor is substituted by a device based on the Venturi effect to minimize the acquisition, maintenance and operating costs associated to the aeration of the reactor. Interestingly, it was found that this aerator can super saturate in oxygen the solution thanks to the formation of air bubbles. The catalytic effect of carbon black (CB) and/or polytetrafluoroethylene (PTFE) to increase the production of H₂O₂ was studied, observing a synergistic effect when the CB/PTFE mixture was deposited on the carbon felt cathode. Efficient hydrogen peroxide generation was obtained at 15 mA cm⁻²: instantaneous production rate of around 9.2 mg H₂O₂ h⁻¹ cm⁻² and a corresponding current efficiency in the order of 90%. The limiting current density increased when the jet aerator was used thanks to i) the super saturation of the solution (dissolved oxygen + air bubbles) and ii) the ability of the CB/PTFE modified carbon felt to use them as oxygen source. The jet aerator is rather promising for the electrochemical generation of hydrogen peroxide.

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1. Introduction

The hydrogen peroxide (H₂O₂) is a versatile and interesting compound with many different domestic and industrial applications [1]. At present, this compound is mainly obtained industrially by the anthraquinone oxidation process with a significant environmental impact derived from the use of organic solvents, metal catalysts and considerable amounts of energy [2,3]. Because of this, novel and cleaner methods are of great interest.

An interesting alternative is the electro-synthesis by means of the two-electron pathway oxygen reduction reaction (ORR). The ORR is a multi-step reaction following a complex mechanism which, despite its importance in different areas of the electrochemistry, has not been fully understood yet [4,5]. In a simplified way, the reaction can proceed directly via 4 e⁻ (Eq. (1)) to water or via 2 + 2 e⁻ also to water, but yielding hydrogen peroxide as stable intermediate (Eq. (2)) [5]:



Carbonaceous materials exhibit a high overpotential for the 4 e⁻ pathway, probably because of the difficulties in breaking down the strong O=O bond (498 kJ mol⁻¹) [4,5], and the ORR reaction proceeds mainly via 2 e⁻ pathway in those materials [6]. Different carbonaceous cathodes have already been tested for the electro-generation of hydrogen peroxide from ORR, namely graphite [6–8], carbon cloth [9], carbon sponge [9,10], reticulated vitreous carbon [6,11,12] or carbon felt [6,9,13]. It is worth mentioning that an interesting catalytic effect have been obtained in those electrodes fabricated by mixtures of carbon and polytetrafluoroethylene [13–16].

For an adequate performance of the cathodic material, oxygen has to be adequately supplied to its surface. In fact, one of the major limitations of the reduction of oxygen to produce hydrogen peroxide is the low solubility of the oxygen in water, around 8 mg dm⁻³ under room conditions [6,8,17]. Because of this, the way in which the oxygen is supplied to the system is critical in the development of H₂O₂ electrolyzers.

The most straightforward solution is the bubbling of atmospheric air directly to saturate the solution. Those systems may

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suffer from important mass transfer limitations, normally leading to low limiting current densities. An increase in the saturation level can be obtained, according to Henry's Law [18,19], by increasing the pressure of the system [8]. Nevertheless, both strategies would lead to an increase in the operating and investment costs of the technology.

Another interesting and widely applied approach for the electro-generation of H_2O_2 are the so-called gas diffusion electrodes (GDEs) [15,20,21]. In this aeration system, the electrode (solid) is placed in between the electrolyte (aqueous) and the air inlet (gaseous) acting as a three-phase contactor. This way, the oxygen is supplied directly to the triple interphase without the need for it to be dissolved in the electrolyte, so that, mass transfer resistance is minimized [22]. Thus, moderate-to-high current densities with acceptable current efficiencies are achieved, even using atmospheric air as oxygen source [23]. However, the generous air flow needed to prevent percolation of water through the electrode surface utilization efficiencies lead to very low oxygen utilization efficiency ($< 1\%$ [24]) which results in a waste of energy and over-sizing of compressors in the event of potential industrial application [25,26].

In any case, all the previous reactor designs for electro-generation of hydrogen peroxide with external aeration include a compressor/compressed air. In a previous work [25], we introduced an aeration device based on the Venturi effect to eliminate this need and minimize the costs related to the acquisition, operation and maintenance of the compression system. The jet aerator (JA), interestingly, is able to generate air bubbles and supersaturate in oxygen the electrolyte, thus, potentially enabling the electro-generation of hydrogen peroxide at higher current densities. Because of this positive prospect, the electro-generation of hydrogen peroxide using the JA deserves attention.

In this work, the global objective is the study of the JA as a way to provide the oxygen necessary for the electro-generation of hydrogen peroxide. To do this, the catalytic activity of the flow-through cathode is studied in detail and the effect of the current density is evaluated to find out if the jet aerator can certainly increase the limiting current density for the production of hydrogen peroxide in an electrochemical system.

2. Materials and methods

2.1. Experimental set-up

A schematic representation of the experimental set-up is shown in Fig. 1. A picture and a video clip showing the real experimental set up together can be found as supplementary material in Appendix A.

The installation is operated under discontinuous mode. The electrolyte ($0.05\text{ M Na}_2\text{SO}_4$ at constant $25\text{ }^\circ\text{C}$) is stored in the tank (filled with 1 dm^3) and pumped at a fixed flow rate of $64\text{ dm}^3\text{ h}^{-1}$ to the jet aerator. In this device, the air enters into the system due to a pressure difference. A flow-meter connected to the suction point of the jet aerator enables the measurement of the air-flow. The biphasic electrolyte-air mixture is fed to the electrochemical cell which is equipped with a funnel-like piece to distribute the flow along the cathodic surface. Then, the flow goes through the CF cathode (circular-shape) supplied by the SGL Group (Wiesbaden, Germany) with a geometric active area of 50 cm^2 and a geometric active volume of 20 cm^3 (0.4 cm thickness). After, the electrolyte reaches the anode (IrO_2 -coated titanium electrode with 50 cm^2 of active area supplied by Tianode, India) and leaves the cell by an exit located in its upper part. The current is fed by means of titanium and steel plates acting as current collector in the case of the cathode and the anode, respectively. These current collectors are not in contact with the electrolyte.

2.2. Modification of the carbonaceous materials

Two different procedures were used to add the CB/PTFE mixture to the carbonaceous materials: ultrasonic immersion and hot dripping.

2.2.1. Ultrasonic immersion

In this procedure, the electrode is modified following a similar to the one described originally by Yu [13]. This procedure consists of three steps: 1) Pretreatment: 15 minutes of ultrasound washing in acetone + water + water, followed by drying at $80\text{ }^\circ\text{C}$ for 24 hours; 2) Immersion: the electrode is soaked for 30 minutes in an

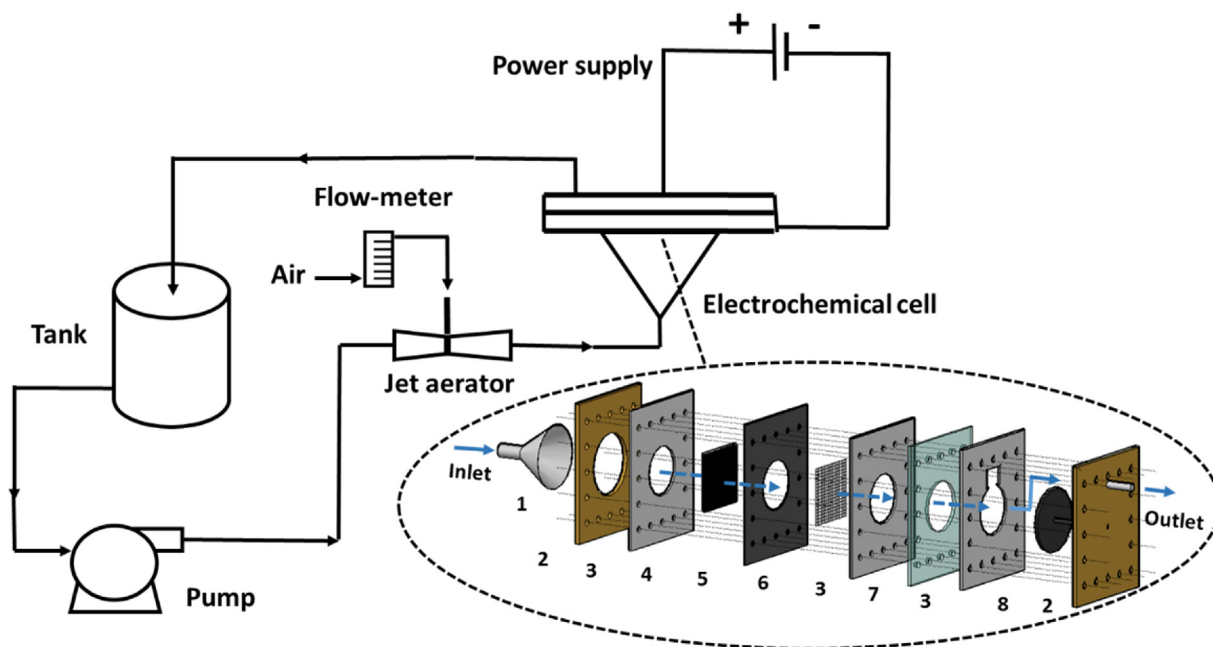


Fig. 1. Experimental set-up. 1. Funnel-like piece 2. Support Plate 3. Rubber gasket 4. CF electrode 5. Titanium current feeder 6. Plastic supporting mesh 7. Metacrylate spacer 8. IrO_2 -based anode.

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