



Electrochemical jet-cell for the in-situ generation of hydrogen peroxide



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ABSTRACT

In this work, a proof of concept of a novel reactor design for the in-situ electrochemical production of H_2O_2 from oxygen reduction reaction is presented for the first time. The innovative design incorporates a venturi-based jet aerator to supply atmospheric oxygen without additional energy consumption to a 3D flow-through modified carbon felt (CF) cathode. Preliminary experiments confirmed that electro-generation of hydrogen peroxide is possible in a system as the one proposed. Comparison with a flow-by cell with a gas diffusion cathode under similar conditions revealed that current efficiency towards hydrogen peroxide accumulation is even higher (72 vs 65% at 1 h) than in the case of the conventional system. Jet aerator stands as a promising oxygen supply thanks to its excellent performance and both low investment cost and energy consumption. Considering all the above, the electrochemical jet cell stands as a rather promising design for the efficient hydrogen peroxide electro-generation.

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1. Introduction

Hydrogen peroxide is a widely used chemical in industries such as textile, pulp and paper bleaching, electronics, metallurgic or environmental applications as it is the case of water treatment, among others. Hydrogen peroxide is mostly manufactured on an industrial scale by means of the Riedl-Pfleiderer process (anthrahydroquinone autoxidation) since its implementation in 1940 by IG FarbenIndustrie [1]. Despite the fact that the yield is high and the process is commercially profitable, it does exhibit various disadvantages in environmental terms on account of its high energy consumption and large amounts of waste generated [2]. In addition, the product has to be transported over long distances from the production point to the end user. An alternative option for the generation of hydrogen peroxide in aqueous medium is the in-situ production from dissolved oxygen reduction reaction (ORR), according to Eq. (1):



This way of production presents various advantages, e.g., ease of automation, mild reaction conditions, its applicability on a small scale and it being fully electricity-powered. Moreover, the electrochemical method avoids all the issues related to transport, storage and handling of this hazardous chemical [3].

The production rate and current efficiency is often limited by the low solubility of oxygen in water which is approximately 40 mg dm^{-3} (oxygen atmosphere) or 8 mg dm^{-3} (air atmosphere) at 1 atm, 25 °C and

deionized water, depending basically on its partial pressure [4]. This problem has been addressed by substituting conventional electrodes for gas diffusion electrodes (GDEs) in which air or oxygen is directly supplied to the cathode without the need for it to be dissolved in the electrolyte [5]. However, O_2 /air utilization efficiencies are extremely small, in the order of <0.1% [6], resulting in a waste of energy and oversizing of compressors in the event of industrial application.

Because of this, an appropriate reactor design is of utmost importance. In the recent years, different authors have proposed novel electrochemical reactors based on flow-through electrodes because of the favorable mass transport rate [7–9]. In the particular case of electrochemical H_2O_2 reactors, it is important to ensure a continuous and sufficient supply of oxygen to the electrode, i.e., minimizing mass transport limitations to the minimum energy consumption and maximum simplicity.

In this work, an innovative approach to electrochemical cell design is presented for the first time. The key feature is a jet aerator to supply oxygen to the system eliminating the need for an external compressor. Also, a 3D flow-through modified carbon felt cathode to achieve high space-time yield is used. With this novel approach to ORR reactor design, higher H_2O_2 generation rate and lower energy consumption is intended compared to conventional GDEs systems.

2. Materials and methods

2.1. Electrolyte solution

All the experiments were performed in a Milli-Q water solution with a concentration of 50 mM Na_2SO_4 as widely used in literature [10–12], supplied by Panreac and a total electrolyte volume of 1 dm^3 .

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2.2. Experimental set-ups

Two different experimental set-ups were used: the novel jet electrochemical cell (henceforth referred to as *jet cell*) and a conventional flow-by cell with a gas diffusion cathode (henceforth referred to as *GDE cell*). A conceptual picture of both cells is shown in Fig. 1.

In both electrochemical cells, a modified carbon felt (CF) electrode was used as the cathode. The electrode was modified following a similar procedure to the one described by Yu et al. [11] which mainly consists in immersing a carbon felt piece into an ink in an ultrasonic bath. The composition of the ink was slightly modified with respect to Yu's and follows the receipt: 10 mg/mL-H₂O of carbon black (Vulcan® XC72R), 50 mg/mL-H₂O of polytetrafluoroethylene (60% Teflon® emulsion solution from ElectroChem, Inc.) and 20 mL/L-H₂O of *n*-butanol. On its part, a titanium anode with active coating based on iridium oxides (Tianode, India) was used as counter electrode. Apart from the cell, each bench-scale installation is properly configured with auxiliary equipment (reservoir tanks, power supply, pump, rotameter, etc.)

2.3. H₂O₂ measurement

The hydrogen peroxide concentration was measured by the potassium titanium (IV) oxalate method [13] according to standard DIN 38 409, part 15, DEV-18. The titanium solution was supplied by Fluka and the absorbance was determined at $\lambda = 407$ nm by means of an Agilent 300 Cary series UV-vis spectrophotometer.

3. Theory

The design of the novel electrochemical jet cell incorporates a key feature with the objective of enhancing efficiency of hydrogen peroxide electro-generation: a venturi-based jet aerator as oxygen supply to a 3D flow-through modified carbon felt cathode with high space-time yield.

Regarding the former, a jet aerator is used to create a suction that entrains air into the water flow. This form of aeration does not need extra equipment, such as a compressor, representing a huge advantage with

respect to conventional GDE systems because of the savings in investment and operating costs. Because of the high velocity in the throat of the jet aerator, the bubbles are broken into smaller pieces as a consequence of the high shear rates [14]. A fraction of the air flow sucked in the system is dissolved, saturating water in oxygen, while the rest of it remains undissolved in the form of air bubbles. This way, the water is supersaturated, i.e., it contains a concentration of oxygen higher than the one of the equilibrium described by Henry's law for a short period of time.

For hydrogen peroxide electro-generation, the oxygen supplied to the system must also be in contact with electrons and protons at some point, according to Eq. (1). The physical place where those three reagents coincide can be referred to as triple-contact point (TCP). An adequate cathode must provide a large surface area with many TCPs where reactants are supplied in sufficient quantities. Considering this, a graphite felt was selected as the cathode material since it possesses a large three-dimensional surface [10,11]. Nevertheless, the H₂O₂ generation rate was reported to be low in bare graphite felt, requiring changes to increase its productivity. Yu et al. reported a simple method to modify this material, adding a carbonaceous powder (carbon black) and polytetrafluoroethylene (PTFE) as a hydrophobic agent [11]. By doing this, the surface area is increased [7] (and so do TCPs) and hydrophobicity facilitates gas diffusion into the inner parts of the porous structure favoring the oxygen supply to active sites. The last property is truly important since hydrogen peroxide electro-generation kinetic from ORR is normally limited by the low concentration of oxygen in water [4] and, thus, being O₂-mass transfer controlled [15]. To minimize this limitation, the water flow is forced to pass through the porous structure of the cathode, as shown in Fig. 1.

These special hydrodynamic conditions are used to achieve a high space-time yield in small concentrations of reactants by creating favorable mass transport conditions [7–9]. In fact, at similar linear empty tube flow velocities, the mass transport coefficient is expected to be 5 to 6 times higher than for a plate electrode with parallel flow [16]. All the aforementioned characteristics configure a promising reactor design for fast and efficient hydrogen peroxide electro-generation.

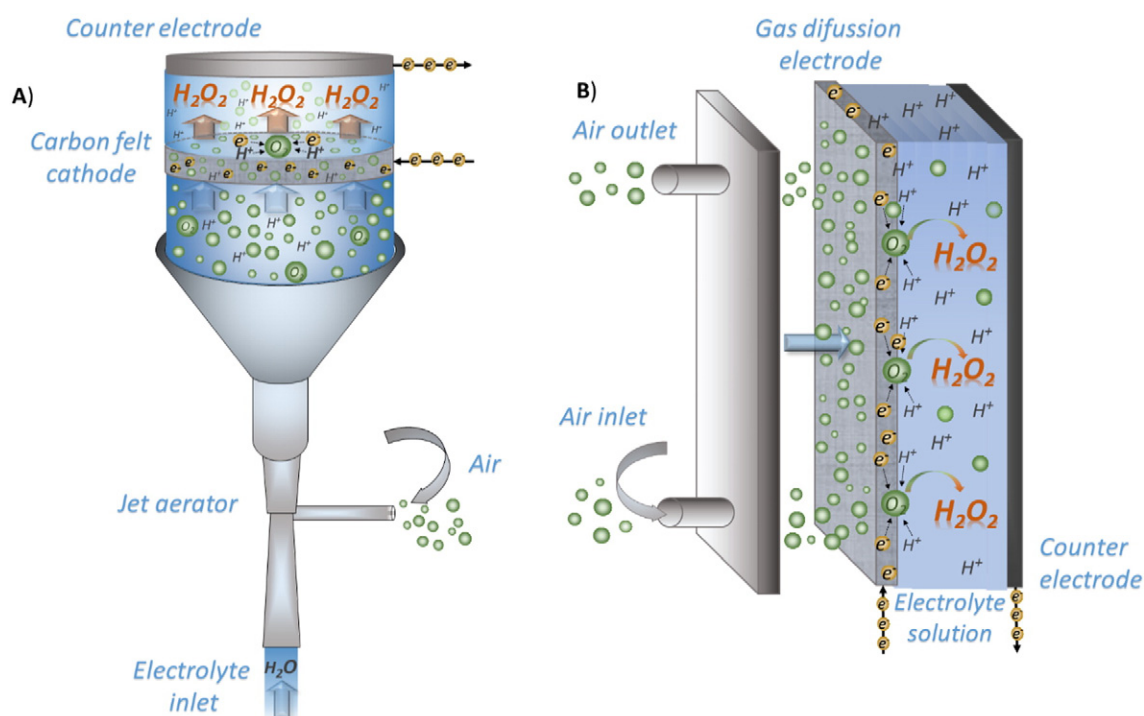


Fig. 1. Conceptual picture of the electrochemical reactors. A) Jet cell B) GDE cell.

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