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The pressurized jet aerator: A new aeration system for high-performance H_2O_2 electrolyzers

J.F. Pérez, J. Llanos, C. Sáez*, C. López, P. Cañizares, M.A. Rodrigo

Chemical Engineering Department, Facultad de Ciencias y Tecnologías Químicas, University of Castilla-La Mancha, Edificio Enrique Costa Novella, Av. Camilo José Cela no 12, 13071 Ciudad Real, Spain

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ABSTRACT

The transport of oxygen to the cathodic surface is a key factor in the rapid and efficient electrogeneration of H_2O_2. In this work, a new aeration system is presented: the pressurized jet aerator, which is characterized by the synergistic coupling of a pressurized circuit with a jet aerator. Under the same liquid flow and pressure, this aerator significantly increases the oxygen mass flow supplied to the system. At 160 $dm^3\,h^{-1}$ and 6 bar, the aeration capacity of the setup including the jet aerator is three times greater than the pressurized system without it (21.9 vs. 7.6 $g\,O_2\,h^{-1}$). The aeration capacity of the jet increases with pressure and a greater oxygen flow is aspired (5.7 vs. 14.2 $g\,O_2\,h^{-1}$, at 1 and 6 bar, respectively) at the same liquid flow (160 $dm^3\,h^{-1}$), thanks to the higher gas density. This system can also collect O_2 evolved at the anode, providing up to 50% of the stoichiometric requirement, thus valorizing a by-product and reducing the energy required for pressurization. H_2O_2 is generated more rapidly in the proposed system than in either the jet aerator under room conditions or in the pressurized system without a jet, demonstrating the power and potential of this system to aerate high-performance H_2O_2 electrolyzers.

1. Introduction

Hydrogen peroxide (H_2O_2) can be electrogenerated by the oxygen reduction reaction on carbonaceous cathodes, as demonstrated as early as 1882 by M. Traube [1,2]. Over the years, this synthetic route has been used for the in situ preparation of aqueous solutions for different purposes [2–5], to enhance the production of peracetic from acetic acid [6,7] and, especially, in electro-Fenton and related technologies [8–10].

Considerable effort has been devoted to the study of the cathodic material and the operational conditions [11–14] while relatively little attention has been paid to the design of the aeration system. It is a point that deserves consideration, given that one of the main limiting factors for fast and efficient electrogeneration of H_2O_2 is the low solubility of oxygen in water under room conditions ($\approx$0.25 mM/8 mg dm^{-3}) [15,16]. The most direct solution is to bubble the gas into the electrolyte. However, the low concentration of oxygen also results in slow oxygen transfer to the cathode. A number of different reactor configurations have been designed to increase oxygen transfer under these conditions, including parallel-plate microfluidic cells [17] and rotating-disk reactors [18].

An alternative approach is to feed the gas directly to the cathode, as in gas diffusion electrodes (GDEs) [19–21]. This solution minimizes mass transfer limitations and yields much better results but still has some drawbacks, such as low oxygen utilization and the need to use a compressor during operation to maintain the delicate equilibrium of pressures at both sides of the electrode [2].

An interesting and little explored method of enhancing the solubility of oxygen in water is the use of pressurized systems [22,23]. In a previous work [24], our group, in collaboration with Scialdone's team, reported a dramatic increase in production rate and current efficiency with pressure. At 30 bar and 100 $mA\,cm^{-2}$, hydrogen peroxide was electrogenerated at 1.84 $mmol\,cm^{-2}\,h^{-1}$ (the highest reported so far in an undivided cell fed with air) with an instantaneous CE of 98.9%, achieving a maximum concentration of 225 mM (7650 $mg\,dm^{-3}$). Despite the fact that 100 $mA\,cm^{-2}$ may be regarded as an industrially relevant current density [2,23,24], the application of this level of pressure might compromise the economic viability of the process at an industrial scale [25].

In all the systems described so far, the external aeration has been carried out by means of a compressor. In previous works [15,26] we reported the use of a jet aerator, a compressor-free system based on the Venturi effect, to supply oxygen to H_2O_2 electrolyzers. Interestingly, this system is able to super-saturate the electrolyte with respect to the intake pressure thanks to the formation of air bubbles, increasing

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* Corresponding author.
E-mail address: Cristina.saez@uclm.es (C. Sáez).

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oxygen transfer to the cathode and, thus, the rate of production of H_2O_2 [26]. Other researchers have also concluded that the use of oxygen in the form of bubbles is positive for H_2O_2 electrogeneration [12,16,27]. However, efficient production was sustained only up to 15 mA cm^{-2} and higher working current densities would be desirable to reduce the size of the reactor.

In this work, a novel aeration system enabling H_2O_2 electrolyzers to achieve high oxygenation capacities at moderate pressures is presented. It involves the combination of a pressurized setup with a jet aerator to create a new and powerful system: the pressurized jet aerator (PJA). In this prototype, the PJA is coupled to a microfluidic flow-through cell [28]. However, the aeration system may also be useful in other types of H_2O_2 electrolyzers which use trickle-bed reactors with co-current liquid/gas to feed fixed [2,23,29–32] or fluidized cathodes [16], as well as in other electrochemical processes involving gas reactants such as CO_2 reduction for carbon valorization [33,34] or the HyS (Westinghouse) cycle for H_2 production [35,36].

2. Materials and methods

2.1. Experimental set-up

A schematic diagram of the experimental setup is shown in Fig. 1. The tank, the cell and most of the pipelining were fabricated from polyvinyl chloride (PVC), except for the connection of the jet with the tank, which was fabricated from Tecalan®. The biphasic tank is half-filled with pressurized air (represented in green) and electrolyte (blue) which is pumped through a jet aerator (throat diameter = 4 mm) using a Micropump® GB – P25 J F5 S A head coupled to a DB 380 A 24 V motor with speed control 0–5 V DC supplied by Techma GPM s.l.r. (Milan, Italy). The electrochemical reactor is a home-made microfluidic flow-through cell [28] in which the electrodes are separated by a thin (150) μm insulating layer of polytetrafluoroethylene (PTFE). The cell is equipped with a mixture of carbon black/polytetrafluoroethylene deposited on a 40 ppi Duocell® aluminium foam (5 mm thickness) as the cathode and a DSA® mesh as the anode (both 33 cm^2 geometric wet area).

2.2. Mass flow calculation

The total oxygen mass flow (m_{O_2}, total) is calculated as the sum of oxygen dissolved in water (m_{O_2}, liquid) plus the oxygen in the gas phase (m_{O_2}, jet).

$$m_{O2,\mathrm{total}} = m_{O2,\mathrm{liquid}} + m_{O2,\mathrm{jet}} \tag{1}$$

$$m_{O2,\mathrm{liquid}} = Q_{\mathrm{liquid}}\cdot[O_2] \tag{2}$$

$$m_{O2,\mathrm{jet}} = Q_{\mathrm{gas}}\cdot\rho\cdot\%(O_2,\mathrm{air}) \tag{3}$$

where Q_{liquid} is the flow measured in the liquid rotameter ($dm^3\,h^{-1}$), $[O_2]$ is the equilibrium concentration at each pressure (g O_2 dm^{-3}) and 25 °C estimated by Henry's law [24], Q_{gas} is the flow measured in the gas rotameter ($dm^3\,h^{-1}$), ρ is the density of air under calibration conditions (1.29 g dm^{-3}) and % (O_2, air) is the percentage of oxygen in air (21%).

3. Results

The key feature of the PJA system is connecting the intake of the jet aerator to the biphasic reservoir tank, as shown in Fig. 1, which allows the system to be pressurized. When liquid flows through the Venturi, the difference of pressure between the tank and the throat of the jet serves as the driving force (ΔP) to aspire the gas. As a result, a pressurized liquid–gas mixture is obtained. It is important to highlight that the aspiration must be in the upper part of the reservoir, which must not be full of liquid. Otherwise, the jet aerator could not draw the gaseous reactant.

3.1. Oxygenation capacity of pressurized jet aerator

As briefly discussed in the introduction, the supply of oxygen is key to the fast and efficient electrogeneration of hydrogen peroxide. Fig. 2(a) shows the total oxygen mass flow at 1 and 6 bar of air pressure when the jet is closed (dotted line) or open (solid line) for different liquid flow rates. It is important to highlight that m_{O_2}, liquid was calculated theoretically as indicated in Section 2, whereas m_{O_2}, jet was measured experimentally by means of the gas rotameter shown in Fig. 1.

In general, m_{O_2}, total increases with liquid flow. In the cases when the jet is closed, m_{O_2}, liquid varies linearly with liquid flow. For a fixed value of liquid flow, m_{O_2}, liquid also varies linearly with pressure, given that the solubility of oxygen in water increases linearly at low pressures, according to Henry's Law [24,37]. Unfortunately, at higher

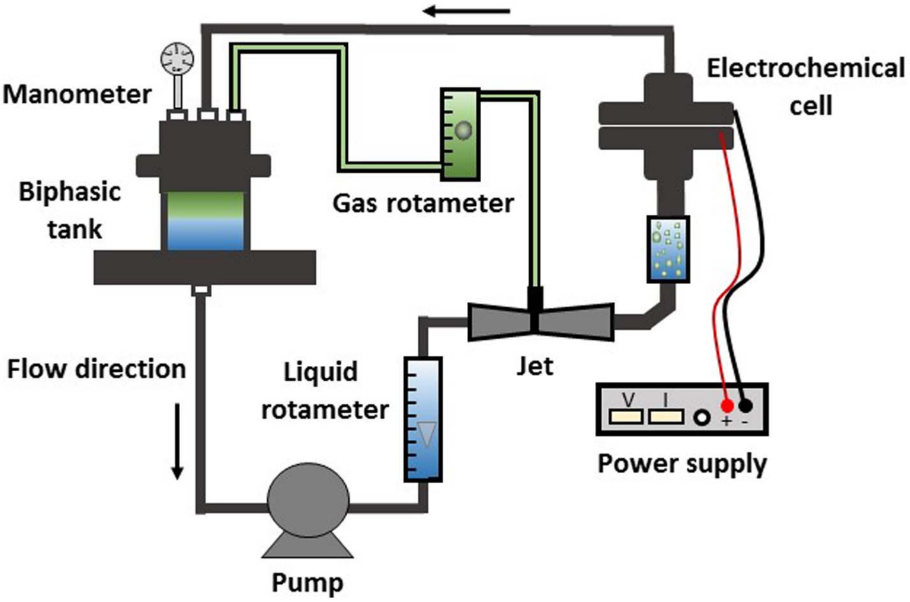

Fig. 1. Schematic representation of the experimental set up.