The pressurized-jet aerator: a new aeration system for high-performing H₂O₂ electrolyzers

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Abstract

The oxygen transport to the cathodic surface is a key aspect for a fast and efficient electro-generation of H₂O₂. In this work, a new aeration system is presented: the pressurized jet aerator. It consists in the synergistic coupling of a pressurized circuit with a jet aerator. Under the same liquid flow and pressure, it increases significantly the oxygen mass flow supplied to the system. At 160 dm³ h⁻¹ and 6 bar, the aeration capacity of the setup including the jet aerator is three times superior to the system pressurized without it (7.6 vs. 21.9 g O₂ h⁻¹). The aeration capacity of the jet increases with pressure and higher oxygen flow is aspired (5.7 vs. 14.2 g O₂ h⁻¹, at 1 and 6 bar respectively) at the same liquid flow (160 dm³ h⁻¹) thanks to the higher gas density. This system can also collect evolved O₂ in the anode which may account up to 50% of the stoichiometric needs, valorizing a by-product and reducing energy consumption for pressurization. H₂O₂ is generated faster in comparison to the jet aerator under room conditions and the pressurized system without jet, which demonstrates the powerfulness and potentiality of this system to aerate high-performing H₂O₂ electrolyzers.

Keywords: aeration system, electrochemical, hydrogen peroxide, jet, pressure

1. Introduction

Hydrogen peroxide (H_2O_2) can be electro-generated by oxygen reduction reaction on carbonaceous cathodes as demonstrated early in 1882 by M. Traube [1, 2]. Over the years, this synthesis route has attracted interest for *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].

A considerable effort has been devoted to the study of the cathodic material and operational conditions [11-14] but, comparatively, considerably less 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 a fast and efficient electro-generation of H_2O_2 is the small solubility of oxygen in water under room conditions ($\approx 0.25 \text{ mM} / 8 \text{ mg dm}^{-3}$) [15, 16]. The most immediate solution is bubbling directly the gas in the electrolyte. However, the low concentration of oxygen also results in slow oxygen transfer to the cathode. Different reactor configurations has been proposed to increase the oxygen transfer under these conditions, as for example parallel-plate microfluidic cells [17] a rotating-disk reactor [18]

A different approach consists in feeding the gas directly to the cathode as in gas diffusion electrodes (GDEs) [19-21]. This solution minimizes mass transfer limitation and yield much better results but still present some drawbacks such as low oxygen utilization and the need of using a compressor during the whole operational time to maintain a delicate equilibrium of pressures at both sides of the electrode [2].

An interesting and scarcely explored alternative to enhance 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 reported a dramatic increase in production rate and current efficiency with pressure. At 30 bar and 100 mA cm^{-2} , hydrogen peroxide was electro-

generated at $1.84 \text{ mmol cm}^{-2} \text{ h}^{-1}$ (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 ($7,650 \text{ mg dm}^{-3}$). Despite the fact that 100 mA cm^{-2} may be regarded as an industrially-relevant current density [2, 23, 24], the application of such pressure might compromise the economic viability of this process on an industrial scale [25].

In all the systems described so far, the external aeration is carried out by means of a compressor. In previous works [15, 26] we reported the use of the jet aerator, a compressor-less 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 oxygen transfer to the cathode and, thus, H_2O_2 production rate [26]. Other researchers also concluded that the use of oxygen in the form of bubbles is positive for H_2O_2 electrogeneration [12, 16, 27]. However, the efficient production was sustained 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 for H_2O_2 electrolyzers to achieve high oxygenation capacities at moderate pressures is presented. It consists in the union of a pressurized setup with the 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, it is interesting also for other H_2O_2 electrolyzers designs 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 electro-chemical 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 scheme of the experimental setup can be found in Figure 1. The tank, the cell and most of the pipelining was fabricated in polyvinyl chloride (PVC), except for the connection of the jet with the tank that was fabricated in (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 0-5V DC supplied by Techma GPM s.l.r. (Milan, Italy). The electro-chemical 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 Duocell® aluminium foam 40 ppi (5 mm thickness) as the cathode and a DSA® mesh as the anode (both 33 cm^2 geometric wet area).

Figure 1. Schematic representation of the experimental set up

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 ($m_{O_2,jet}$).

$$m_{O_2,total} = m_{O_2,liquid} + m_{O_2,jet} \quad [1]$$

$$m_{O_2,liquid} = Q_{liquid} \cdot [O_2] \quad [2]$$

$$m_{O_2,jet} = Q_{gas} \cdot \rho \cdot \% (O_2, air) \quad [3]$$

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 of the PJA system is connecting the intake of the jet aerator to the biphasic reservoir tank, as shown in Figure 1. In this manner, the system can, indeed, be pressurized. When liquid flows through the Venturi, a difference of pressure appears between the tank and the throat of the jet serving 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 and that it cannot 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 for a fast and efficient electro-generation of hydrogen peroxide. Figure 2.a shows total oxygen mass flow for pressures for 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 the $m_{O_2,liquid}$ was calculated theoretically as indicated in Section 2 whereas $m_{O_2,jet}$ was measured experimentally by means of the gas rotameter shown in Figure 1.

Figure 2. Oxygenation capacity of the system at different liquid flow rates and pressures a) ■ 1 bar ▲ 6 bar; b) ■ O_2 dissolved ■ O_2 in bubbles; $Q_{liq} = 160 dm^3 h^{-1}$.

In general, $m_{O_2, total}$ increases with liquid flow. In the case of working with the jet 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 solubility of oxygen in water increases linearly according to Henry's Law at low pressures [24, 37]. Unfortunately, at higher pressures ($P > 10$ bar), the solubility does not longer increases linearly so the increase of pressure is progressively less effective in aerating the system. In economic terms, energetic costs for compression increases with pressure. With regard to processing equipment, as a rule of thumb it can be considered that materials and apparatus can withstand positive pressures up to 10 bar without much additional capital investment [25]. At greater pressures, thicker-walled and more expensive equipment are necessary, thus operate at values greater than 10 bar must be justified (for detailed calculations, see Appendix A of this reference [25]). All the aforementioned reasons seem to advice against using high pressures in H_2O_2 electrolyzers.

However, when the jet aerator is open, $m_{O_2, total}$ increases exponentially with liquid flow (see Figure 2.a) because higher velocities leads also to higher ΔP between the throat and the tank. This effect is present from $100 dm^3 h^{-1}$ on, because lower values of liquid flow does not create a significant ΔP in the jet used in this study. As an example, values of

$m_{O_2,total}$ equal to 7.6 and 21.9 g O₂ h⁻¹ were calculated at 6 bar and 160 dm³ h⁻¹ for closed/open jet, respectively, which implies an improvement of approximately 3 times. It is important to highlight that even if the use of the jet aerator implies a pressure drop of the fluid stream, it allows an important increase of oxygen mass flow without the need to increase the operating and design pressure of the system. Indeed, to achieve an oxygen mass flow of 21.9 g O₂ h⁻¹ without the jet, an air pressure of approximately 17-18 bar would be needed.

The use of a pressurized system together with the jet has another important advantage. Figure 2.b shows the contribution of the dissolved oxygen ($m_{O_2,liquid}$, bottom part of the column) and air bubbles generated in the jet ($m_{O_2,jet}$, top part of the column) to $m_{O_2,total}$ at a fixed liquid flow. Interestingly, $m_{O_2,jet}$ also increases with pressure from 5.7 at 1 bar to 14.2 g O₂ h⁻¹ at 6 bar. This effect may be explained considering that the higher density of the gas under pressure results in a higher mass flow at a given value of liquid flow (i.e. ΔP in the jet).

On top of what have been discussed previously, the use of hermetic systems, pressurized or not, present another positive feature. Those systems can collect the oxygen evolved in the anode from water/H₂O₂ oxidation. This is an interesting way of making the most of a by-product and reduce the energy consumption required for pressurization. It should not be considered as a negligible contribution because it can provide up to 50% of the stoichiometric oxygen required in the cathode.

3.2 Effect of aeration on H₂O₂ generation

Hydrogen peroxide was electro-generated in the system under different aeration conditions. A high current density was selected in such a way that the production of H₂O₂ is limited by oxygen mass transfer to the cathodic surface.

Figure 3. Concentration of H₂O₂ vs. time under different aeration conditions. $j = 60 \text{ mA cm}^{-2}$; Cathode volume = 16 cm^3 ; $Q = 160 \text{ dm}^3 \text{ h}^{-1}$; $T = 25 \text{ }^\circ\text{C}$; $V_0 = 2.25 \text{ dm}^3$; Electrolyte: Na₂SO₄ 0.05 M.

Under room pressure and jet closed, H₂O₂ reaches a low concentration of 2.4 mg dm^{-3} after 20 minutes, slightly increasing up to 4.0 mg dm^{-3} under jet aeration after next 20 minutes of electrolysis. A further accumulation, up to 12.5 mg dm^{-3} , is observed when the electrolysis is run in a pressurized system at 6 bar. Interestingly, a considerably higher concentration (33.4 mg dm^{-3}) is measured using the PJA. The slopes of the graph clearly shows that H₂O₂ is produced faster using the PJA in comparison to both jet aeration and pressurized system with the jet closed. Those results are in accordance with the aeration capacity shown in Figure 2 and demonstrate the effectiveness of the PJA as a powerful aeration system.

Considering the positive perspectives of the PJA, future work will be devoted to the production of H₂O₂ and its application to as for example electroFenton process for wastewater treatment.

4. Conclusions

From this work, the following conclusions can be drawn:

- A pressurized system can be coupled to a jet aerator following the layout shown in this work
- The union is clearly synergistic. The oxygen mass flow in the mono-phasic pressurized system increases up to 3 times using the jet aerator.
- The jet aerator is more efficient under pressure given that it is able to aspire larger oxygen flows because of the higher density of the gas.
- Evolved O₂ in the anode can be collected in a hermetic system as the one presented here, potentially covering up to 50% of the O₂ needs for the production of H₂O₂.
- Hydrogen peroxide is generated faster using the PJA in comparison to both jet at room pressure and the pressurized system.
- The PJA is a powerful aeration system able to supply high oxygen flow rates at moderated pressures

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