Mass transport studies during dissolved oxygen reduction to hydrogen peroxide in a filter-press electrolyzer using graphite felt, reticulated vitreous carbon and boron-doped diamond as cathodes

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ABSTRACT

This paper describes the mass transport characterization of oxygen reduction reaction (ORR) to yield hydrogen peroxide at porous electrodes like graphite felt (GF) and reticulated vitreous carbon (RVC, 45 pores per inch) and at a boron-doped diamond (BDD) plate in the presence of a plastic net. A filter-press electrolyzer was used for the reduction of 0.24 mM of O_2 in the presence of 0.5 M of either Na_2SO_4 or 0.5 M $NaClO_4$ as supporting electrolytes in water at pH 2.8. Linear differential pulse voltammetry (LDPV) was performed at different volumetric flow rates in the range 25.3–50.6 $cm^3 s^{-1}$. Cathodic polarization curves using GF, RVC and BDD revealed that ORR is limited by mass transport at $-0.4 < E < -0.1$ V vs SHE in sulfate medium. However, in perchlorate medium, such limitation appeared at $-0.8 < E < -0.5$ V, $-0.5 < E < -0.25$ V, and $-0.3 < E < -0.25$ V using GF, RVC and BDD, respectively. From these analyses, limiting current intensities were measured and used to obtain the mass transport correlation, $k_m a = bu^c$. The values of constant b, which is related to mass transport properties, shape and cell dimensions, were between 0.0012–0.0028, 0.011–0.170 and 0.0007–0.0006 for GF, RVC and BDD, respectively. The constant c exhibited values of 1.47–1.56 and 0.80–0.93 for GF and RVC, as a result of chaotic flow pattern inside the porous structures, and 0.84–1.00 for BDD plate employing the turbulence promoter. Mass transport of O_2 depends on the electrode geometry, thus highlighting that the flow pattern is a complex function of the specific surface area and the electrode porosity.
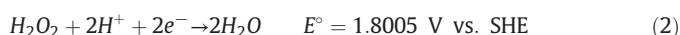
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1. Introduction

In recent years, several electrochemical advanced oxidation processes (EAOPs) such as electro-oxidation, electro-Fenton (EF) and photoelectro-Fenton (PEF) have been proposed as promising environmental remediation technologies to develop appropriate treatments for the removal of refractory organic matter from wastewater [1–6]. In this context, there exists increasing interest in the in-situ electrogeneration of hydrogen peroxide by means of oxygen reduction in acidic solutions containing Fe^{2+}, aiming to implement the Fenton-based electrochemical processes to treat wastewater containing organic pollutants [7]. One key aspect to be addressed in the EF process regards the effectiveness and efficiency of the cathodic production of H_2O_2 according to the following reaction [8]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad E° = 0.927 \text{ V vs. SHE} \tag{1}$$
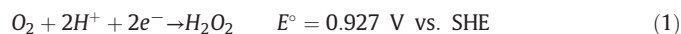
So far, carbonaceous materials such as graphite, graphite felt (GF), reticulated vitreous carbon (RVC), activated carbon fiber (ACF), carbon nanotubes, boron-doped diamond (BDD) and gas diffusion electrode (GDE) have been tested as cathode [8–12], confirming that they possess some advantages such as non-toxicity, good stability, acceptable conductivity and enough chemical resistance [13].

It is well known that during the oxygen reduction reaction (ORR), H_2O_2 becomes accumulated at the cathode–solution interface and may be partially decomposed as shown in reaction (2). Hence, the particular hydrodynamics inside filter-press cells might enhance the mass transport of H_2O_2 from the electrode surface toward the bulk, thus minimizing the extent of that undesired reaction. In addition, protons may compete for electrons as well, therefore promoting the hydrogen evolution reaction (HER) (3). Reactions (2) and (3) are detrimental, since they cause a decrease in the current efficiency of ORR to yield H_2O_2. In conclusion, studies on mass transport, as well as on potential and current distribution, are mandatory to enhance the current efficiency [14].

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \qquad E° = 1.8005 \text{ V vs. SHE} \tag{2}$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad E° = 0.245 \text{ V vs. SHE} \tag{3}$$

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Several authors have focused on the physical and chemical modifications of raw carbonaceous materials to enable a higher efficiency of ORR [10–12,15,16]. In contrast, the mass transport characterization during the reduction of oxygen is rather scarce, despite being a very useful tool for evaluating the performance of filter-press electrolyzers, which is a fundamental task for envisaging their scale-up [17].

Under mass-transport controlled conditions, that is to say, within the limiting current *plateau* region, the current intensity is related to the global mass transport coefficient, $k_m a$ [18]:

$$k_m a = \frac{I_L}{nFCV_R} \quad (4)$$

where a is the volumetric area, i.e., A/V_R, being A the electrode surface area and V_R the electrolyte volume inside the porous electrode matrix as occurs in GF and RVC, for example; for a BDD plate, V_R considers the electrolyte volume between electrodes in the presence of a plastic net used as turbulence promoter [17,19]. The limiting current is denoted by I_L, n is the number of the electrons exchanged during the electrochemical reaction under study, F is Faraday's constant and C is the concentration of electroactive species in the bulk.

Eq. (4) is valid if there are no significant changes in C. This is achieved by recording cathodic polarization curves (I vs E, using potentiodynamic techniques) at different flow rates. From the resulting values of I_L, an empirical power law equation can be obtained to characterize the mass transport dependence relative to the electrolyte flow rate [17,18]:

$$k_m a = b u^c \quad (5)$$

where u is the mean linear flow velocity (in $cm^{-1} s$) and the constants b and c are determined experimentally, being associated with the flow channel shape, electrode form, cell dimensions, transport properties and electrolyte hydrodynamics [17]. The product $k_m a$ is typically used for reactors with porous electrodes because it is well known that only a fraction of the electrode area is used during the electrochemical process.

This paper presents the mass transport characterization during the cathodic reduction of dissolved oxygen to produce hydrogen peroxide using a well-engineered flow cell like the FM01-LC laboratory reactor equipped with a BDD plate, GF or RVC as cathode [17]. Polarization curves (I vs E) were recorded at different flow rates in order to obtain the I_L values and thus, the mass transport correlations. The influence of perchlorate and sulfate as supporting electrolyte anions was also examined.

2. Materials and methods

2.1. Chemicals

All solutions were prepared with analytical grade reagents from Sigma Aldrich and deionized water. Two different supporting electrolyte solutions, namely 0.5 M $NaClO_4$ and 0.5 M Na_2SO_4, both at pH 2.8, were used. The dissolved oxygen concentration was kept at 0.24 mM (7.8 mg L^{-1}) with continuous air feeding.

2.2. Instruments

An SP 150 BioLogic® potentiostat–galvanostat coupled with a Booster VMP3B-10 from BioLogic® and run with EC-Lab® software was used for all electrochemical experiments. The dissolved oxygen concentration was determined by means of a Hanna® HI 9142 dissolve oxygen meter. The continuous oxygen supply during the electrochemical tests to maintain the desired dissolved oxygen concentration was ensured upon air sparging into the solution reservoir with a Sunny® SP 1500 air pump at 2 $dm^3 s^{-1}$. The H_2O_2 concentration accumulated in electrolyzed solutions was determined using the light absorption of the titanic-hydrogen peroxide colored complex at $\lambda = 408$ nm [20], using a Perkin Elmer Lambda 35 UV/Vis spectrophotometer.

2.2.1. Flow cell experiments

The filter-press cell employed in this work was the FM01-LC reactor, which is widely described in detail in the literature [17,19]. BDD, GF, and RVC were employed as cathodes, and a platinized titanium plate was used as anode. BDD plates with 2–7 mm thickness supported on Ti and $10–100 \times 10^{-1} \Omega^{-1} cm^{-1}$ electrical conductivity were provided by Metakem™. RVC 45 pores per inch (ppi) with 0.5 cm thickness and $10–100 \times 10^{-1} \Omega^{-1} cm^{-1}$ electrical conductivity was supplied by Electrosynthesis Company. GF with 0.4 cm thickness and $10–100 \times 10^{-3} \Omega^{-1} cm^{-1}$ electrical conductivity was provided by ROOE Group. A stainless steel plate of 4 cm in height, 16 cm in length and 0.3 cm in thickness was used as cathodic collector in the case of GF and RVC. The electrical contact was made by gluing RVC and GF onto the current collector with conducting carbon cement (Leit-C from Agar Aids). When using the BDD plate, a plastic routed mesh, promoter type D, was used as turbulence promoter between the anode and cathode [17,19]. The characteristics and main parameters of the FM01-LC reactor and electrodes are shown in Table 1. The undivided FM01-LC cell had a single electrolyte compartment and a flow circuit operating under recirculation batch mode [19].

The electrode potentials inside the electrolyzer were measured against a saturated calomel electrode (SCE) when using $NaClO_4$ as the supporting electrolyte, whereas a saturated sulfate reference electrode (SSE) was used when Na_2SO_4 was employed. Both reference electrodes were inserted into a Luggin capillary. Note that all electrode potentials shown in this work are referred to a standard hydrogen electrode (SHE).

2.2.2. Cathodic polarization curves for the oxygen reduction reaction (ORR)

The limits of potential and current density where oxygen reduction takes place to produce hydrogen hydroxide in the filter-press cell were determined by linear differential pulse voltammetry (LDPV) at different flow rates (25.3, 31.5, 37.9, 44.2 and 50.6 $cm^3 s^{-1}$) owing to the very small dissolved oxygen concentration (0.24 mM at 32 °C). This technique allows distinguishing more easily the capacitive current, which becomes more relevant at dilute concentration ($<10^{-4}$ M) of electroactive species. For GF and BDD electrodes, the cathodic potential was swept from open circuit potential to -0.9 V vs SHE in both, perchlorate and sulfate media, at a potential sweep rate of 5 mV s^{-1}, with a pulse height of 10 mV and a pulse width of 100 ms. After several trials, the potential sweep rate for the RVC electrode was set to 1 mV s^{-1}, with a pulse height of 1 mV and a pulse width of 50 ms, since the previous parameters did not allow observing the mass transport *plateau* with enough precision. Nevertheless, it is important to

Table 1
FM01-LC reactor parameters and cathode characteristics.

Electrode height (B)	4.0 cm
Electrode spacing (S)	0.55 cm
Electrode length (L)	16.0 cm
Volumetric area graphite felt (GF) (a)	517.0 cm^{-1}
Volumetric area reticulated vitreous carbon (RVC) 45 ppi (a)	29.5 cm^{-1}
BDD plate electrode area	64.0 cm^2
Turbulence promoter	Plastic mesh D; DC^a and $DL^b = 11.0$ mm 0.83 (overall voidage)
GF	0.40 cm (thickness), 0.97 (overall voidage)
RVC	0.50 cm (thickness), 0.90 (overall voidage)
Volumetric flow rates (Q)	25.3–50.6 $cm^3 s^{-1}$ (16.2–32.5 cm s^{-1} for GF; 14–28 cm s^{-1} for RVC; 13.8–27.6 cm s^{-1} for BDD)

[a] DC = internal dimension of the short diagonal of the mesh.
[b] DL = internal dimension of the long diagonal of the mesh.