



On the ability to electrogenerate hydrogen peroxide and to regenerate ferrous ions of three selected carbon-based cathodes for electro-Fenton processes



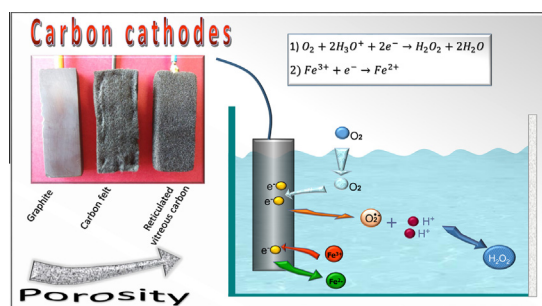
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HIGHLIGHTS

- Three different carbon-based cathodes for electro-Fenton processes were studied and compared.
- Hydrogen peroxide electrogeneration and iron reduction were assessed.
- The effect of operative conditions was investigated.
- RVC exhibited superior electrocatalytic ability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 June 2015

Received in revised form 9 August 2015

Accepted 10 August 2015

Available online 14 August 2015

Keywords:

Reticulated vitreous carbon electrode

Carbon felt electrode

Graphite electrode

Hydrogen peroxide production

Iron reduction

Electro-Fenton

ABSTRACT

This paper compares three different carbon-based materials as cathodes in electro-Fenton processes. In particular, we investigated a graphite, a carbon felt (CF) and a reticulated vitreous carbon (RVC) electrode with a focus on both electrogeneration of hydrogen peroxide and reduction of ferric ions. The influence of the operative parameters such as current intensity, pH, temperature and feeding gas was studied by conducting galvanostatic electrolyses in a two-compartment reactor separated by a cationic membrane. The dissolved oxygen concentration was optimized and monitored.

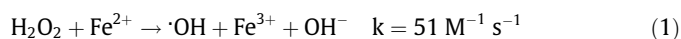
The results obtained showed that all the cathodes presented good ability to electrogenerate hydrogen peroxide. Unlike graphite, the tridimensional electrodes exhibited superior performances in air flow and the possibility to adopt higher currents. Interestingly, their behavior differed significantly in the electroregeneration of ferrous ions. In this case, RVC and CF presented efficiencies and reduction rates higher than graphite and resulted almost unaffected by the operative conditions.

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1. Introduction

The ferrous iron-mediated decomposition of hydrogen peroxide under acidic conditions is known as Fenton reaction, after the scientist who first, in the late nineteenth century, used these reagents to oxidize tartaric acid [1]. Although the mechanism is still debated

[2], it is widely accepted that, according to what was found by Haber and Weiss [3], the reaction proceeds through the formation of hydroxyl radicals:



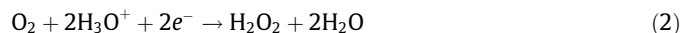
Hydroxyl radicals, with a standard potential of 2.8 V and a half lifetime of about 10^{-9} seconds, enable fast and non-selective oxidation of a wide range of molecules of environmental concern. The development of an electrochemical process capable of

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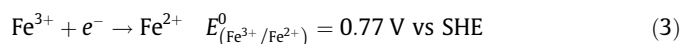
producing the Fenton reagent at selected cathodes has overcome the main drawbacks represented by the need of notable amounts of reagents and the overproduction of iron-containing sludge. Due to the results obtained, this technology has experienced a fast development and its applications over the years have ranged from treatment of dyes [4–6], pesticides [7,8] herbicides [9], explosives [10], surfactants [11], drugs [12,13], real effluents [14–16] and spent adsorbent regeneration [17].

In particular, the in situ electrogeneration of hydrogen peroxide, obtained by oxygen reduction on carbon electrodes (Eq. (2)), avoids all the issues related to transport, storage and handling of a hazardous chemical:

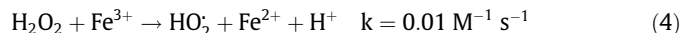


Moreover, it has been previously reported that electrogenerated H_2O_2 , due to the synergetic effect of different radical species produced during oxygen reduction, results in faster and more effective oxidation than the commercial product [18], which is often stabilized to reduce catalytic decomposition induced by transition metals and contaminants in trace.

A further advantage resulting from electro-Fenton processes can be attributed to the simultaneous occurrence of iron regeneration, via cathodic reduction, that allows the use of quasi-catalytic amounts of this reagent with limited production of sludge and great economic benefits:



Although also ferric iron is capable of promoting a Fenton-type reaction (Eq. (4)), the active species generated, the hydroperoxyl radical, presents an oxidizing power so weak ($E^0 = 1.65 \text{ V vs SHE}$) that it can be considered unreactive toward organic molecules [19]:



Thus, to obtain fast oxidation is necessary to favor the reduction of iron III to iron II by accelerating, if possible, this reaction, which is significantly slower than the backward process. Therefore, the performance evaluation of a cathode material for electro-Fenton processes should account for two different abilities: the capability of reducing oxygen to electrogenerate hydrogen peroxide and that of reducing ferric ions to restore ferrous ions thus promoting the reaction leading to $\cdot\text{OH}$ production. It is widely accepted that the electrogeneration of hydrogen peroxide, either for electro-Fenton application or for direct oxidation and disinfection, successfully occurs on carbon-based cathodes due to their high overpotential toward water discharge. An extensive literature is available ranging from traditional electrode materials such as graphite [20–22], graphite felt [23] to less investigated cathodes including carbon sponge [24], activated carbon fiber [25] as well as novel modified electrode [26,27].

Among them, gas diffusion electrodes (GDEs) exhibit the highest efficiency in the H_2O_2 production [28,29] also when air was used as feeding gas [21] even in high salinity medium [30]. Their better performance can be easily explained by considering that their structure enables to overcome the limitations related to oxygen solubility and transport. Similar encouraging results can be also achieved by adopting electrodes with enhanced reactive area and porosity as in the case of carbon felt (CF) [31–33] and reticulated vitreous carbon (RVC) [34–36]. The use of these materials is further promoted by their attractive properties, especially cheapness, possibility of construction in different shapes, lightness, thermal and chemical resistance [37]. On the other hand, it has been shown that for the purposes of electro-Fenton process an overproduction of hydrogen peroxide can result counterproductive [18] either by favoring the occurrence of parasite reactions to detriment

of the hydroxyl radical electrogeneration or by limiting iron regeneration when the process is current controlled. Most of the literature considers H_2O_2 electrogeneration, and only a limited number of papers deal with Fe^{2+} regeneration [38–40], though both reactions are crucial for the success of electro-Fenton process and the Fe^{2+} regeneration is thermodynamically disadvantaged [20].

In this paper the performance of three of the commonest carbon materials, namely graphite, carbon felt and reticulated vitreous carbon has been evaluated and compared. To determine their suitability as cathodes in electro-Fenton processes the influence of the main operating parameters in both hydrogen peroxide electrosynthesis and iron regeneration has been separately investigated.

2. Materials and methods

2.1. Apparatus and procedures

Electrochemical tests were conducted in a Perspex® two-chamber cell separated by a Nafion 324 cation exchange membrane; each chamber contained a volume of solution of 100 ml and was stirred with a magnetic bar. The experiments were carried out under galvanostatic conditions using a potentiostat AMEL 2051.

The anode was a platinum disk with a surface of 5 cm^2 . Different parallelepiped-shaped cathodes were tested: a 100 ppi RVC electrode (ERG Aerospace Corporation, Oakland CA), a graphite electrode (Carbone Lorraine, France), a CF electrode (Carbone Lorraine, France); each one was properly prepared in order to have a submerged geometric surface of $2 \times 2.5 \times 1 \text{ cm}$ (Fig. 1).

Oxygen or air (Unistar air pump 2000-2) were continuously supplied during the tests as dissolved oxygen (DO) sources at a flow of 200 ml min^{-1} unless differently specified. To achieve stable and reproducible DO concentrations, the sparging of air or oxygen started 20 min before the beginning of each electrolysis.

Sodium perchlorate 0.01 M was used as supporting electrolyte in the anodic compartment (pH = 6.1).

Tests were performed at different temperature conditions by means of a recirculating water bath.

All the runs were performed under constant agitation of 1250 rpm and repeated at least three times.

DO measures were conducted in the same apparatus, in the absence of a current flow, using distilled water.

Hydrogen peroxide production tests were performed in the cathodic compartment. The catholyte consisted of 100 ml of a $\text{Na}_2\text{SO}_4/\text{NaHSO}_4$ buffer solution at three different pH values: 2,

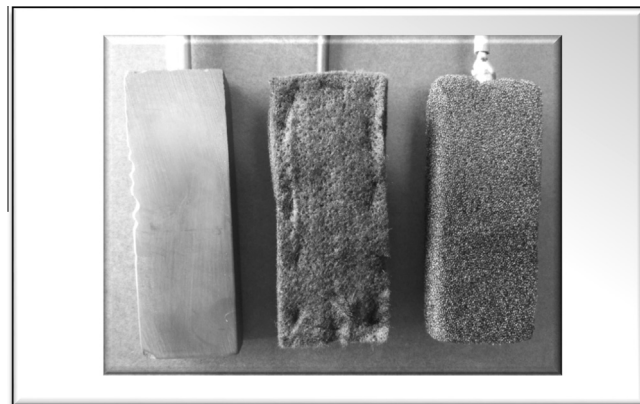


Fig. 1. Electrodes used in the experiments. From left to right: graphite, carbon felt and reticulated vitreous carbon cathode.

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