



An energy-saving production of hydrogen peroxide via oxygen reduction for electro-Fenton using electrochemically modified polyacrylonitrile-based carbon fiber brush cathode



Guangsen Xia, Yonghong Lu, Haibo Xu *

Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao, Shandong 266100, China
College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao, Shandong 266100, China

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ABSTRACT

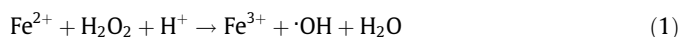
A polyacrylonitrile-based carbon fiber brush (PAN-CFB) was electrochemically modified and efficiently used as cathode for H₂O₂ electrogeneration in electro-Fenton process. H₂O₂ generation performance and energy consumption for PAN-CFB cathode before and after modification were evaluated and compared. For electrochemically modified PAN-CFB (EMPAN-CFB) cathode, the maximal H₂O₂ concentration (approx. 80 mg L⁻¹ by 1000 C charge, >90% current efficiency) appeared at −0.4 and −0.5 V vs. SCE, a ca. 500 mV positive shift compared with the pristine one, showing desirable stability without performance decay after 30 cycles utilization. Moreover, the influence of the distance between anode and cathode as well as the electrolyte concentration on the energy consumption for H₂O₂ generation was investigated, with obviously reduced energy consumption for the EMPAN-CFB cathode. Finally, methyl orange was decolorized via electro-Fenton process using the EMPAN-CFB cathode and rapid color removal was accomplished in 5 min following the pseudo-first-order kinetic model with high correlation.

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1. Introduction

Electro-Fenton process is an environmental-friendly, efficient and promising advanced oxidation process applied in effluent disposal [1–3], and has been widely investigated for degradation of various model organic contaminants (e.g. dyes [4–6], phenolic compounds [7–9], etc.) or real wastewater [10,11]. In the process, the in-situ electrogenerated H₂O₂ via cathodic oxygen reduction reacts with Fe²⁺ externally added or from iron anode in acidic solution to produce ·OH (Eq. (1)), a powerful oxidizing radical which can non-selectively decompose most organics and convert them into small molecules or CO₂, H₂O and inorganic ions [12–14]. The performance of electro-Fenton process depends on the H₂O₂

concentration electrogenerated on cathode via 2-electron oxygen reduction reaction (ORR) (Eq. (2)) [15], and therefore an efficient cathode material is necessary and crucial to the electro-Fenton process.



Carbon-based materials, e.g. graphite [16], carbon fiber [17], activated carbon fiber [18], carbon sponge [19], carbon nanotube [20], carbon nanotube sponge [21], carbon black (acetylene black [22], Vulcan XC-72 R and Printex L6 [23]) are the most widely used cathodes due to the advantages of commercial availability, high conductivity, stability and ORR activities with high hydrogen evolution overpotential, chemical resistance and no toxicity [12,14]. To further enhance their 2-electron ORR activity and current efficiency of H₂O₂ electrogeneration, many researches have been done to modify the cathode materials. Quinones compounds [24–28], metal-phthalocyanine [29–31], rare-earth-derived compounds [32], hydrazine hydrate-ethanol [9,33], carbon nanotube [14,34], polypyrrole composite film [4,35,36] and polyaniline [37] were used as modifier or as electrocatalyst directly mixed with carbon material or coated on the cathode surface. Other attempts such

Abbreviations: CE, current efficiency; EC, energy consumption; EMPAN-CFB, electrochemically modified polyacrylonitrile-based carbon fiber brush; HER, H₂ evolution reaction; LSV, linear sweep voltammetry; MO, methyl orange; ORR, oxygen reduction reaction; PAN-CF, polyacrylonitrile-based carbon fiber; PAN-CFB, polyacrylonitrile-based carbon fiber brush; PES, polyethersulphone; SCE, saturated calomel electrode.

* Corresponding author at: Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao, Shandong 266100, China.

E-mail address: xuwangri@163.com (H. Xu).

as plasma pretreatment method [38], electrodeposition method [14] have also been made. However, these modifications are often expensive and complex with multiple steps. Besides, the energy consumption for H_2O_2 electrogeneration via 2-electron ORR was seldom evaluated or investigated with very high value (e.g. $22.2 \text{ kW h kg}^{-1} \text{ H}_2\text{O}_2$) [30]. Therefore, it is significant to enhance electrode performance via simple modification method for energy-saving production of H_2O_2 which is promising for industrial application.

Previously, polyacrylonitrile-based carbon fiber brush (PAN-CFB) was suitably used as electro-Fenton cathode and its high catalytic activity toward 2-electron ORR was demonstrated [17,39]. Here EMPAN-CFB cathode modified by electrochemical galvanic pulse method was used and anticipated to achieve higher current at less negative applied potential which would significantly decrease the energy consumption in large-scale H_2O_2 production.

2. Experimental

2.1. Preparation and electrochemical modification of cathode

All chemicals used were analytical grade without further purification. T300-12 K polyacrylonitrile-based carbon fiber was purchased from Xiangsheng carbon fiber plant (Yancheng, China) and was made into brush electrode. The brush of 30 mm in diameter and 180 mm in length was constructed as previously described with a titanium wire (TA2, $\Phi 1 \text{ mm}$) current collector and about 2 g carbon fiber wires [17].

PAN-CFB was electrochemically modified in a two-electrode cell containing $2 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution using a DC power supply (Fig. 1(I)) via recurrent galvanic pulses at room temperature, cycling 6 times from an anodic current of 3.5 A for 300 s to a cathodic current of -3.5 A for 300 s. Two PAN-CFB electrodes were alternatively used as anode and cathode during modification process with the changing current direction.

2.2. LSV measurement

In order to evaluate the ORR activity, linear sweep voltammetry (LSV) curves of PAN-CFB and EMPAN-CFB cathode were tested in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ ($\text{pH} = 3$) at room temperature by an electrochemical workstation (Zahner IM6ex, Germany), using a three-electrode cell with a PAN-CFB or EMPAN-CFB cathode as working

electrode, a $6 \text{ cm} \times 4 \text{ cm Ti/IrO}_x\text{-TiO}_2\text{/IrO}_2$ mesh anode as counter electrode, and saturated calomel electrode (SCE) as reference electrode (Fig. 1(II)). Prior to test, 99.9% N_2 or air was bubbled for 20 min to saturate the solution and continuously bubbled throughout the measurement.

2.3. Electrogeneration of H_2O_2

Electrogeneration of H_2O_2 was carried out at constant current or potential controlled by ZF-9 potentiostat/galvanostat (Shanghai Zhengfang Electric Appliance Co. Ltd) in the same three-electrode system as above (Fig. 1(II)). Different distances between the anode and the cathode were adopted and described in the figure caption. The performance of the brush cathode before and after modification under acidic, neutral and alkaline conditions were investigated respectively in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ ($\text{pH} = 3$ and 7) and $0.1 \text{ mol L}^{-1} \text{ NaOH}$ ($\text{pH} \approx 13$) solutions. The initial pH of Na_2SO_4 solution was measured with a pH-meter (Mettler Toledo Delta-320) and the required pH values were adjusted using dilute H_2SO_4 and NaOH solution prior to electrolysis. The initial pH of NaOH solution was about 13 and was not further adjusted. During electrolysis, air was fed into by an air pump at a flow rate of 3 L min^{-1} to supply the dissolved oxygen needed for ORR. All potentials were relative to SCE potential.

2.4. Decolorization of methyl orange in electro-Fenton process

The electro-Fenton process for decolorizing model pollutant—methyl orange (MO) was performed in a two-electrode cell using $\text{Ti/IrO}_x\text{-TiO}_2\text{/IrO}_2$ mesh anode and EMPAN-CFB cathode (Fig. 1(III)) in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution containing $25 \text{ mg L}^{-1} \text{ MO}$. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was used as Fe^{2+} sources to participate in Fenton reaction. The samples at different electrolysis time were taken out and were filtered by $0.45 \mu\text{m}$ polyethersulphone (PES) membranes (Germany Membrane Co.) for analysis, recording the UV-Vis spectra of filtrates by a UV-Vis spectrophotometer (Shimadzu UV 2450, Japan) equipped with 10 mm quartz cuvettes.

2.5. Analytical procedure

The H_2O_2 concentration was determined by UV 2450 spectrophotometer at 400 nm, using the potassium titanium (IV) oxalate ($\text{C}_4\text{H}_2\text{O}_9\text{Ti}$) method [40]. The current efficiency (CE) of H_2O_2 generation is defined as follows (Eq. (3)):

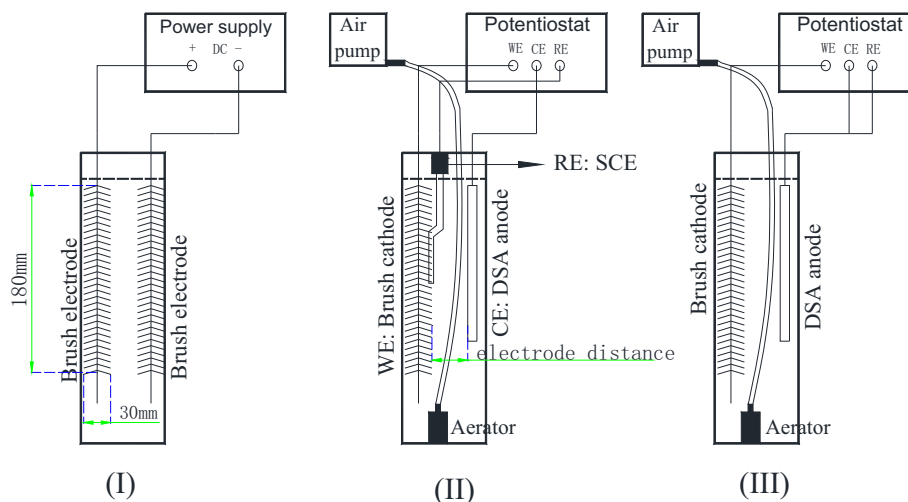


Fig. 1. Schematic of the electrolytic system used for (I) electrochemical modification of PAN-CFB electrode (II) H_2O_2 electrogeneration and (III) electro-Fenton process.

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