



Electrogeneration of hydrogen peroxide for electro-Fenton system by oxygen reduction using chemically modified graphite felt cathode

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ABSTRACT

A simple chemical method using hydrazine hydrate as the main reagent was firstly used to modify graphite felt as cathode for efficient electro-Fenton process. The influences of the different concentration of hydrazine hydrate were comparatively studied on the yield and current efficiency of H₂O₂ production, confirming that the modified cathode had much higher electrocatalytic activity. The optimum concentration of the hydrazine hydrate was 10%, and the yield of H₂O₂ was as 2.6 times as that without modification under the same conditions. The cyclic voltammetry analysis indicated that the modified cathodes exhibited stronger current responses and more negative hydrogen evolution potentials than the unmodified one. The operational parameters such as cathodic potential, pH and O₂ flow rate were optimized for the efficient H₂O₂ electrogeneration. The maximum accumulation of H₂O₂, up to 247.2 mg/L, was obtained at −0.75 V (vs. SCE) and O₂ flow rate of 0.4 L/min. The influence of pH on the yield of H₂O₂ was slight, but it was obvious on current efficiency. The modified cathode was confirmed to be more efficient in degradation of *p*-nitrophenol by electro-Fenton process at both acidic and neutral pH, indicating the positive effect of chemical modification onto the performance.

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1. Introduction

As an environmentally friendly electrochemical technology, electro-Fenton (EF) process is a promising method for degradation of refractory pollutants in aquatic environment [1,2]. The EF process is based on the continuous in situ electrogeneration of H₂O₂, which can eliminate acquisition, shipment and storage, along with the addition of iron catalysts to produce powerful oxidant ·OH. Therefore, the major concern with the EF system relates to the improvement of H₂O₂ production. Carbonaceous materials are widely used as cathodes due to the advantages such as no toxicity, good stability, high conductivity, and low catalytic activity of H₂O₂ decomposition [2]. Recently, several carbonaceous electrodes have been reported such as graphite [3], reticulated vitreous carbon [4,5], activated carbon fiber [6,7], carbon sponge [8], carbon/graphite felt [9–13] and carbon/PTFE composite electrodes [14–16]. For more efficient usage of these carbonaceous materials in EF system, it is crucial to improve the oxygen reduction reaction (ORR) for H₂O₂ production, which is a typical two-electron transfer process, as shown in the following equation:



Various modification attempts have been made to enable cathode more efficient for H₂O₂ production and EF process, such as rare-earth-derived compounds modification [17], 2-ethylanthraquinone modification [18], coating the polypyrrole composite film [19], and oxygen or nitrogen functionalization [20,21]. Although carbon/graphite felt has been considered not so efficient as carbon/PTFE composite in the production of H₂O₂ [22], their large 3D active surface, mechanical integrity and easy acquisition still make it a promising cathode material [2]. In addition, there is still room to improve the electrocatalytic activities of the carbon/graphite felt. Chemical modification is a simple and efficient way to improve the electrochemical activity of the carbonaceous electrodes by changing their surface functional groups. The surface area, surface functional groups and degree of graphitization of the carbonaceous material vary with the different modified processes [23].

Aiming to improve the in situ production of H₂O₂ at graphite felt cathode for EF system, hydrazine hydrate–ethanol system was firstly used to modify these carbon materials in our study. The influences of the different compositions of the hydrazine hydrate–ethanol system were comparatively studied on the yields and current efficiency of H₂O₂ production. The operational parameters such as cathodic potential, pH and O₂ flow rate were also investigated for the efficient H₂O₂ electrogeneration. In addition, the electrocatalytic performance in EF system before and after

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cathode modification was evaluated by degradation of *p*-nitrophenol (*p*-Np). As common persistent organic contaminants and typical biorefractory organic compounds, nitrophenols are important raw materials for production of pesticides, herbicides, explosives, dyes, and pharmaceuticals [24], and thus have been chosen as target pollutants in many researches [25–29].

2. Experimental

2.1. Cathode modification

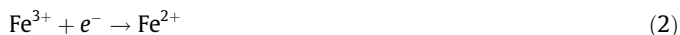
All chemicals used in this study were analytical grade and used as received without further purification. The graphite felts (Shanghai Qijie Carbon material Co., Ltd.) with a specific surface area of about 0.6 m²/g were degreased in an ultrasonic bath with acetone and deionized water in sequence, dried at 80 °C for 24 h, and then annealed at 150 °C for 2 h. These pretreated materials were marked as CF. A series of modified electrodes were chemically modified as follow. The pretreated graphite felts were immersed in 100 mL mixture of ethanol and hydrazine hydrate, and after refluxing at 60 °C for 6 h, the samples were annealed at 150 °C for 2 h. Since the volume concentration of the hydrazine hydrate in the mixture were 5%, 10%, 15% and 20%, the modified electrodes were marked as CF-HA-5%, CF-HA-10%, CF-HA-15% and CF-HA-20%, respectively.

2.2. Electrogeneration of H₂O₂

The H₂O₂ electrogeneration experiments were performed in a 0.13 L undivided three-electrode cell using CHI660D electrochemical workstation (CH Instruments, Chenhua, Shanghai, China). The prepared cathode (5 cm × 2 cm) was used as working electrode, a platinum wire as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The distance between the working electrode and counter electrode was 3.5 cm. An aqueous solution of 0.05 M Na₂SO₄ was used as supporting electrolyte and the pH was adjusted by H₂SO₄ or NaOH. Prior to the electrolysis, oxygen (96% purity) was bubbled near the cathode at a desired flow rate for 20 min, and then oxygen reduction was performed at different potentials on the working electrode for 120 min, with a constant magnetic stirring of 300 rpm. At 20 min intervals, 1 mL samples were taken for analyzing the concentration of the H₂O₂, and the electric charges were recorded.

2.3. Degradation of *p*-Np in EF system

The EF process was carried out in the same apparatus, using *p*-Np (initial concentration 50 mg/L) as model pollutant, and still 0.05 M Na₂SO₄ was added as supporting electrolyte. The solution pH was adjusted by H₂SO₄ or NaOH. In addition, 0.2 mM Fe³⁺ (ferric nitrate) was used as the catalyst instead of Fe²⁺ due to the cathodic electro-regeneration of Fe²⁺, as shown in the following equation:



The *p*-Np samples were taken at an interval of 20 min to determine the degradation efficiency.

2.4. Analytical methods

Cyclic voltammetry (CV) was carried out to compare the electrochemical processes during the H₂O₂ production, and recorded by the CHI660D workstation at a scan rate of 10 mV/s in a three-electrode cell system described previously at ambient temperature. The concentration of H₂O₂ during electrogeneration process was monitored by UV–vis spectrophotometer (UV759, Shanghai instrument analysis instrument Co., LTD.) using the potassium

titanium (IV) oxalate method [30]. The current efficiency (CE) for H₂O₂ production was defined as follow [31]:

$$\text{CE} = \frac{nFC_{\text{H}_2\text{O}_2}V}{\int_0^t I dt} \times 100\% \quad (3)$$

where *n* is the number of electrons transferred for oxygen reduction to H₂O₂, *F* is the Faraday constant (96,486 C/mol), *C*_{H₂O₂} is the concentration of H₂O₂ (mol/L), *V* is the bulk volume (L), *I* is the current (A), and *t* is the time (s).

The concentration of *p*-Np samples was monitored by high performance liquid chromatograph (HPLC, FL2200) with UV detector wavelength at 318 nm. The mobile phase was composed of chromatographically pure methanol and 0.1% H₃PO₄ (v/v) at 40/60. The separation was performed at 35 °C using an TMAQ-C18 column (∅4.6 mm × 250 mm) at a flow rate of 1.0 mL/min. The total organic carbon (TOC) of the initial and final samples in the EF process was determined by a TOC analyzer (Analytikjena multi N/C 3100).

3. Results and discussion

3.1. Effect of the concentration of hydrazine hydrate

Fig. 1 shows the yields of hydrogen peroxide and current efficiencies at different cathodes modified with different concentra-

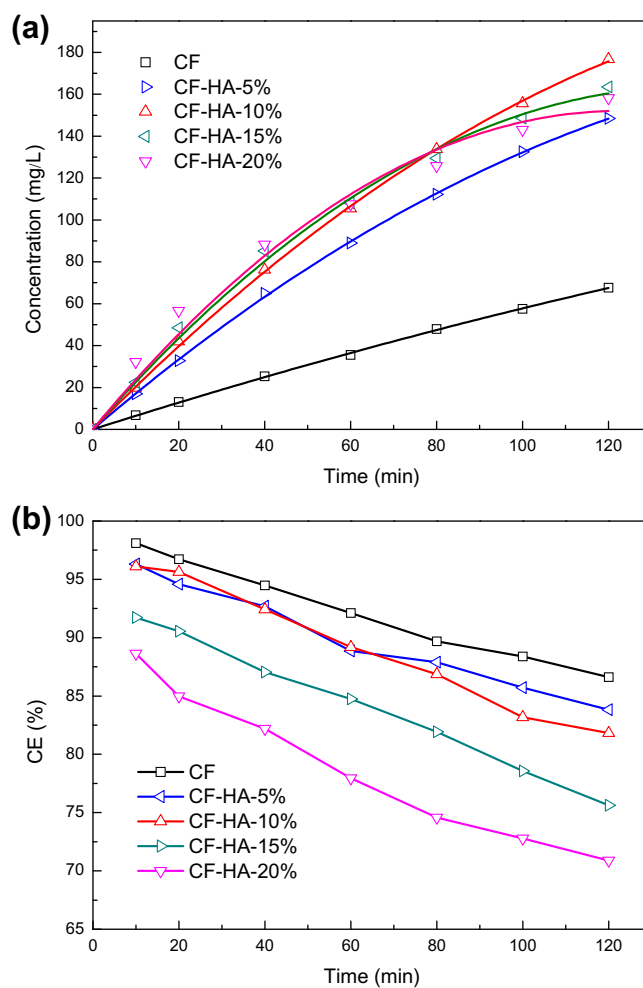


Fig. 1. The effects of the concentration of hydrazine hydrate on (a) the yields of H₂O₂ and (b) current efficiency. Conditions: *E* = −0.65 V (vs. SCE), 0.05 M Na₂SO₄, pH = 6.4, O₂ flow rate at 0.4 L/min.

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