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Novel rolling-made gas-diffusion electrode loading trace transition metal for efficient heterogeneous electro-Fenton-like

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ABSTRACT

A novel rolling-made gas-diffusion electrode loading with trace transition metal (M/GDE, M = Cu, Ce, Mn, Fe, Co) was prepared and used as cathode in heterogeneous electro-Fenton-like (EF-like) for methyl orange (MO) degradation. The rolling-made GDE showed a good activity and stability for H_2O_2 production, with a H_2O_2 concentration of 595 mg/L at 120 min and variation within 3.36% even after 10 times reuses. The effect of five metals and their loading contents on MO degradation were investigated, and the Co/GDE showed the highest activity when the loading content of Co was 0.7 wt%. Particularly this activity showed good stability toward pH variation (3–9), demonstrating promising advantage of this heterogeneous EF-like for application. Further it was proved that hydroxyl radical played an important role on pollutants degradation, and a possible degradation scheme for heterogeneous EF-like on Co/GDE was proposed based on the results and characterizations such as scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and X-ray diffraction (XRD).

1. Introduction

Advanced oxidation processes (AOPs) have attracted more and more attention because hydroxyl radical (•OH) can be produced to degrade recalcitrant organic pollutants that cannot be biologically eliminated in wastewater [1–4]. Electro-Fenton (EF) process is one of the most widely used electrochemical AOPs [5–9]. It can electro-generate H_2O_2 in situ via a two-electron reduction of O_2 on suitable cathode (Eq. (1)) [6].

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

In the homogeneous EF process, Fe^{2+} is usually added externally to react with the electro-generated H_2O_2 to produce •OH (Eq. (2)) and Fe^{2+} can be regenerated on the cathode by Eq. (3) [6].

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \quad (2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (3)$$

Despite its high efficiency, the wide application of homogeneous EF process is limited by some drawbacks, such as narrow working pH range (optimal value 3), generation of abundant sludge in the effluent after neutralization treatment, inconvenient process due to adding iron ions every run [10–12]. Therefore, great efforts have been made to overcome these problems. One effort is to develop heterogeneous EF process, where soluble Fe^{2+} is replaced with Fe-containing solid catalysts, such as Fe-C [13,14], iron oxyhydroxide (FeOOH) [15], iron oxides [16–19] and iron-organic framework [20]. The oxidation of organic pollutants has been attributed to •OH production from the reaction of H_2O_2 with dissolved iron ion and/or surface iron. Iron precipitates can be inhibited and the working pH range can be expanded [19]. Another effort is to develop a Fenton-like system containing other transition metals (e.g., Co, Cu and Ni) and H_2O_2, which also could enlarge the working pH range, as shown in Eq. (4) [21,22].

$$M^{(n-1)+} + H_2O_2 + H^+ \rightarrow M^{n+} + {}^{\bullet}OH + H_2O \quad (4)$$

Where M is the transition metal and n is the charge of the metal ion in an oxidized state.

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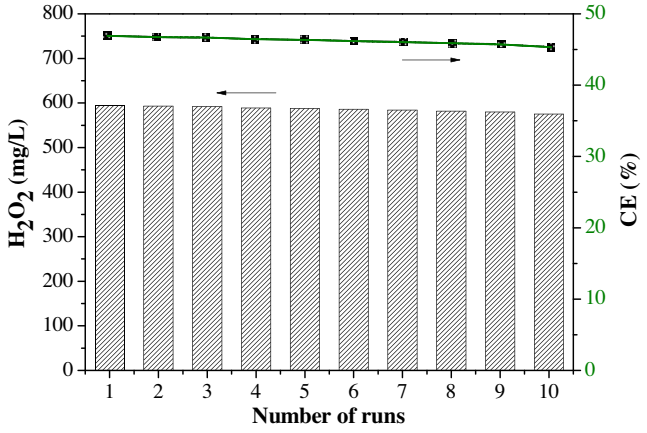

Fig. 1. The stability test of rolling-made GDE in 10-times continuous runs. Conditions: 100 mL, 0.05 M Na_2SO_4, I = 100 mA, pH = 3, air flow rate 0.2 L/min.

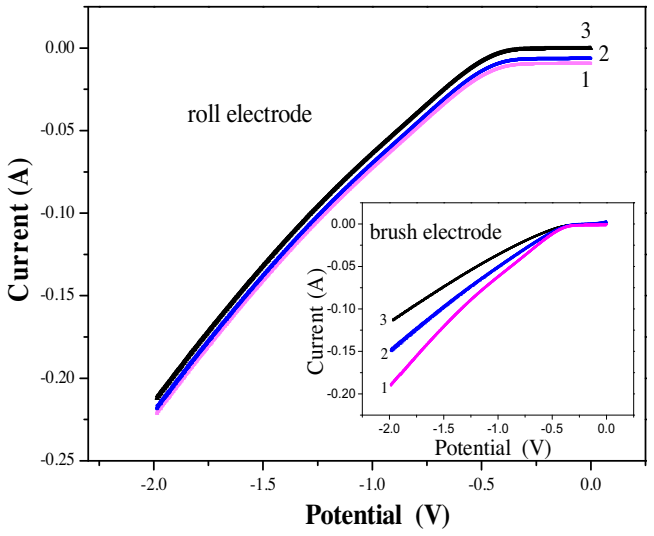

Fig. 2. Linear sweep voltammograms of the rolling-made GDE and brushing-made GDE. Conditions: scanning rate 50 mV/s, 0.05 M Na_2SO_4, pH 7, oxygen saturation.

On the other hand, efficient EF system needs a high electro-generation ability of H_2O_2, which largely depends on the cathode materials. Carbon materials are widely used as EF cathode, such as graphite [23,24], carbon sponge [25,26], carbon or graphite felt [27,28], activated carbon fiber (ACF) [29] and carbon-polytetra-fluoroethylene (PTFE) gas-diffusion electrode (GDE) [30–34]. Among these cathodes, GDE is regarded as the most effective one to produce H_2O_2. Traditional GDEs were made by brushing C-PTFE blend onto carbon cloth several times [13,35]. However, this brushing-made method is coarse and labor-consuming for commercialization. A rolling-made activated carbon-PTFE GDE has been developed and stable in microbial fuel cells [36,37], however, this rolling method has not been attempted in EF system.

In the present work, a rolling-made GDE was developed and its activity and stability for H_2O_2 electro-generation was tested. In order to expand the working pH, the rolling-made GDE loading different metals was designed for the heterogeneous EF-like process. Methyl orange (MO), a model azo dye, was selected as a target contaminant for assessing the performance of this heterogeneous EF-like system. The effect of transit metals, different content of metals loading and pH value were investigated to optimize the working conditions for MO degradation by the heterogeneous EF-like process.

2. Experimental

2.1. Materials

Sodium sulfate anhydrous, cobalt nitrate, cerium nitrate, ferric nitrate, copper nitrate, manganous nitrate, sulfuric acid, sodium hydroxide, ethanol and methyl orange were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used as received without further purification. Carbon black (CB) and PTFE (60 wt%) were purchased from Shanghai Hesen Electric Co., Ltd. All solutions were prepared in de-ionized water.

2.2. Preparation of GDEs and metal/GDEs

The rolling-made GDEs were prepared according to the following procedure: Appropriate amount of CB and ethanol were mixed and sonicated for 30 min, followed by dripping PTFE suspensions (the mass ratio of CB and PTFE was 0.1) into the blend slowly. This step was operated with ultrasonic agitation to disperse CB and PTFE to form fine networks of gas channels. After another 30 min, the blend was dried at 80 °C in water bath until a dough-like paste was formed. The paste was firstly rolled on a roller machine (PX-GY-100, Shenzhen Poxon Machinery Technology Co., Ltd) to form a gas-diffusion film (0.4 mm thickness), and then was rolled on one side of stainless steel mesh to be a flat sheet of 0.4 mm thickness. This side is the so-called diffusion layer. The same procedure was then used to prepare the catalyst layer (the mass ratio of CB and PTFE was 1.0). The catalyst layer was firstly rolled to be a film of 0.4 mm thickness and then rolled on another side of the stainless steel mesh to be a flat sheet of 0.6 mm thickness. At last, the sheet was calcined at 350 °C for 30 min.

Catalysts loading metals were synthesized according to literature with minor modifications [38]. Appropriate amount of CB, metal nitrate salts (M = Cu, Ce, Mn, Fe, Co), deionized water and ethanol were mixed and sonicated for 30 min, then dried overnight at 60 °C in an oven. The mixture was calcined in a tube furnace at 900 °C under N_2 for 2 h.

Table 1
H_2O_2 production performance comparison with literatures.

Cathode material	Experimental conditions	H_2O_2 generation rate (mg/h/cm^2)	EEC (kWh/kg)	OE (%)	CE (%)	References
Graphite	100 mL of 0.1 M Na_2SO_4, pH 3.0, E = −0.65 V vs. SCE, O_2 flow rate 0.33 L/min	1.00		0.04	64 (2 h)	[24]
Carbon sponge	125 mL of 0.05 M Na_2SO_4, pH 3.0, O_2 flow rate 100 mL/min, I = 100 mA	2.84		0.14	18(3 h)	[26]
ACF	500 mL of 0.05 M Na_2SO_4, pH 3.0, O_2 flow rate 0.1 L/min, j = 25 mA/cm^2	0.55		0.13		[29]
GDE	1.5 L of 0.1 M K_2SO_4, pH 1.0, E = −2.25 V vs. SCE	15.52	22.10			[32]
GDE	1 L of 1 g/L Na_2SO_4, pH 3.0, j = 70 mA/cm^2	15.96	25.03		58 (1 h)	[33]
GDE	250 mL of 0.1 M K_2SO_4, pH 1.0, E = −0.60 V vs. Ag/AgCl	10.50	325.2			[34]
GDE	100 mL of 0.05 M Na_2SO_4, pH 3.0, air flow rate 200 mL/min, j = 33 mA/cm^2	10.92	20.84	0.90	47 (2 h)	Present work