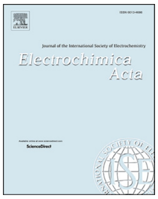
Electrochimica Acta 260 (2018) 112–120

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta



Fabrication of graphene@graphite-based gas diffusion electrode for improving H_2O_2 generation in Electro-Fenton process

Zhihong Zhang [a], Hongshan Meng [b], Yujing Wang [a, *], Limin Shi [a], Xue Wang [a], Shouning Chai [c, **]

[a] School of Materials Science and Chemical Engineering, Xi'an Technological University, Xi'an, Shaanxi 710021, China
[b] School of Civil & Architecture Engineering, Xi'an Technological University, Xi'an, Shaanxi 710021, China
[c] College of Science, Xi'an University of Architecture and Technology, Xi'an, Shaanxi 710055, China

ARTICLE INFO

Article history:
Received 14 July 2017
Received in revised form
21 October 2017
Accepted 8 November 2017
Available online 9 November 2017

Keywords:
Graphene
Gas diffusion electrode
Hydroxyl radical
Electron-Fenton

ABSTRACT

A typical graphene@graphite-based gas diffusion electrode (G-GDE) with high conductivity and remarkable electrocatalytic activity was prepared for the electro-Fenton (E-Fenton) system in order to achieve an efficient degradation for organic pollutants. The G-GDE was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), and nitrogen adsorption-desorption analysis. Continuous on-situ generation of H_2O_2 through an oxygen reduction reaction (ORR) was achieved at the non-metallic G-GDE cathode. Rhodamine B (RhB) was used as a model organic pollutant to evaluate the performance of the E-Fenton system with G-GDE cathode. The effects of pH, Fe^{2+} concentration were investigated. After 60 min, the removal rate reached 98% with G-GDE in the optimal condition, which was higher than that with traditional graphite-based gas diffusion cathode (GDE) and graphite sheet cathode (GE), and the energy consumption with G-GDE was only 84% of that with GDE under the same condition. The calculated electron transfer number (n) of the ORR with G-GDE was 2.1–2.2 in the selected potential range using rotating disk electrode. The results demonstrated that the addition of graphene could enhance the ORR activity by virtues of improving electrochemical conductivity and porous structure. Moreover, excellent corrosion resistance and reuse ability were also presented for the G-GDE electrode. So the G-GDE can be used as a low-cost and efficient cathode material for degradation of organic wastewater in E-Fenton system.

1. Introduction

Electro-Fenton (E-Fenton) process, derived from traditional Fenton reaction, has become one of the most interesting environmental treatments. The main characteristic is that H_2O_2 is supplied continuously through a two-electron of oxygen reduction reaction (ORR) at the cathode as Eq. (1) [1]. H_2O_2 could react with added Fe^{2+} to produce the hydroxyl radical (•OH) as Eq. (2) [2]. The •OH has a high standard potential ($E^{\Theta}(\bullet OH/H_2O) = 2.80$ V versus NHE), which is the second strongest oxidant only next to fluorine. Various organic pollutants could be attacked non-selectively by •OH via electron transfer, electrophilic addition, dehydrogenation, etc., and decomposed to CO_2, H_2O and inorganic ions. Meanwhile, Eq. (2) reaction is maintained by some reduction reactions of Fe^{3+} to Fe^{2+} such as Eq. (3) [3].

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \tag{1}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \bullet OH + OH^- \tag{2}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{3}$$

Notably, the degradation efficiency of E-Fenton is mainly determined by the electrogeneration ability of H_2O_2. How to improve the yield of H_2O_2 is an important factor in the treatment. As is well-known, the kinetics of ORR is strongly dependent on the electrode materials. In recent, carbonaceous materials, such as

---

* Corresponding author.
** Corresponding author.
E-mail addresses: wangyujing1220@126.com (Y. Wang), s.n.chai@xauat.edu.cn (S. Chai).

https://doi.org/10.1016/j.electacta.2017.11.048
0013-4686/

graphite, carbon felt, carbon fiber, boron-doped diamond (BDD), and traditional graphite-based gas diffusion electrode (GDE) have been widely used as cathode for formation of H_2O_2 because of non-toxic, good stability and conductivity. Among of them, GDE is a special porous membrane electrode. Since a large amount of gas can reach the inside of the electrode, and the surface contacts to the electrolyte solution, a three-phase (solid, liquid, gas) membrane electrode can be formed. A large number of pores not only allow the reaction gas to be easily transferred to the electrode, but also which is beneficial to the migration of liquid reactants and products. GDE has attracted much attention due to its high H_2O_2 production, which porous structure is favor of O_2 mass transfer and increases its solubility, resulted in a fast O_2 reduction and high accumulation concentration of H_2O_2. Various derivative GDEs composing of different constitutes have been developed, such as carbon-polytetrafluoroethylene (PTFE) [4], graphite-PTFE [5] [6], PTFE-carbon black [7], etc. Pozzo et al. [4] found that the carbon-PTFE gas diffusion cathode can increase the yield rate of H_2O_2, reaching to 450 mg/L, which is 1.68 times that of graphite electrode under the same condition. Zhou group [5] found that the yield rate of H_2O_2 was up to 45 mg/L on graphite-PTFE GDE at 60 min, much higher than that on graphite electrode. Chen [7] found H_2O_2 concentration can be enhanced substantially, from about 15 mg L^{-1} to more than 500 mg L^{-1}. Previous studies revealed that there are great rooms for improvement of H_2O_2 production if some proper materials were used to prepare GDE.

Graphene is known as an interesting material with advantages of high surface area [8], superior mobility of charge carriers, and excellent mechanical behavior [9]. It has been used in many fields including catalysis [10], electronics [11], energy [12], and sensor [13], etc. The booming development in graphene-based materials has triggered tremendous attention for its environmental applications. Graphene has been demonstrated to being an efficient metal-free ORR catalyst. Consequently, the use of graphene in E-Fenton process was also considered gradually. For example, Cretin et al. [14] prepared a new E-Fenton cathode by deposition of reduced graphene oxide on carbon felt to degrade Acid Orange 7. Compared to raw carbon felt, the degradation rate was significantly enhanced on the composite cathode due to the higher production of H_2O_2. Zhang and co-workers [15] found the thermally reduced graphene coated on the glassy carbon disk exhibited high selectivity for two-electron ORR and high peroxide yield of over 62.5%. And the results revealed that the π bond of oxygen is broken while the σ bond is generally preserved on reduced graphene oxide because of the high free energy change. In addition, it has reported that graphene and its derivatives were efficient in adsorption removal of various pollutants, such as organic dyes, polycyclic aromatic hydrocarbons, antibiotics, even inorganic heavy metal ions due to high specific surface area and a large number of functional groups [16].

Considering its remarkable properties and relatively simple preparation method, graphene as main raw material, was used to prepare a new type of graphene@graphite-based gas diffusion electrode (G-GDE) in this work. The homogeneous E-Fenton process using G-GDE as cathode was applied in the decomposition and mineralization of Rhodamine B (RhB). The removal performance and mineralization capability are compared with graphite-based GDE, and graphite sheet electrode (GE) as cathode in E-Fenton process. The influences of pH, and iron ion concentration on degradation of RhB, as well as the cathode stability were investigated. The proper mechanism for the great enhancement of RhB degradation was analyzed in detail. The G-GDE is expected to be a promising E-Fenton cathode material and it offers possibilities to design new heterogeneous systems for wastewater treatment.

2. Experimental

2.1. Preparation of GO

Graphene oxide (GO) was synthesized by a modified Hummers method. First, graphite powder (3.0 g) together with $NaNO_3$ (1.5 g) were added into concentrated sulfuric acid (160 mL) slowly and stirred for 1 h in ice bath condition. Second, some $KMnO_4$ (9.0 g) was added into the above solution. 2 h later, the mixture was removed from ice bath, heated up to 40 °C and continued to stir up 1.5 h. Then, deionized water (160 mL) was poured into the above mixture solution slowly, and stirred it for 1 h under boiling condition. 30% H_2O_2 (30 mL) and deionized water (175 mL) were added into the above mixture solution when it cooled down below 50 °C. It was filtrated after continuous stirring for 3 h. Finally, the sample was washed with the mass fraction of 10% HCl until there is no sulfuric acid root and with deionized water until pH = 7. Graphene oxide (GO) was obtained.

2.2. Preparation of G-GDE

GO (100 mg) was ultrasonically dispersed into 100 mL H_2O completely. The dispersion was adjusted to pH = 10 with aqueous ammonia of 28 wt%. It was centrifuged for 3 min to eliminate a small quantity of non-stripping GO. Then, 0.2 mL hydrazine hydrate was added into the centrifuged supernatant dispersion at 90 °C and maintained for 2 h to prepare reduced graphene oxide (rGO). In ambient condition, 0.1 g graphene, 0.8 g graphite, and 0.2 g polytetrafluoroethylene (PTFE) were mixed in 160 mL 3 wt% ethanol solution and kept them in water bath at constant 80 °C. The paste mixture was adhered to nickel mesh evenly when it was getting slightly cooled. After a while, the paste was solidified and cold-pressed it 3 min (thickness: *ac.* 0.7 mm). The sample was calcined at 300 °C for 1.5 h, thereby G-GDE was prepared successfully. To eliminate residual surface ethanol and PTFE, the electrode needed to be soaked in fresh acetone 24 h. Only after washed repeatedly with deionized water and dried well, it can be conducted in experiment. As described above, a graphite-based gas diffusion electrode was produced successfully without the addition of rGO. In addition, another comparative electrode used an outsourced graphite electrode.

2.3. Electrode characterization

The structure and morphology of the sample was characterized by scanning electron microscope (SEM) (Quanta 400F, Philip) and transmission electron microscope (TEM) (JEM-2010, Japan). X-ray diffraction (XRD, XRD-6000, SHIMADZU) analysis was performed using a diffractometer with Cu Kα radiation, with the XRD working voltage at 40 kV, tube current of 30 mA, scanning range is 5°–60°, scanning speed at $4° \cdot min^{-1}$. Thermal stability of sample was studied by thermogravimetric analysis/differential scanning calorimetry (TGA/DSC, METILER TOLEDO). Thermal stability of G-GDE was investigated from ambient temperature at a rate of 10 °C min^{-1} to 800 °C. The specific surface area was determined by the BET adsorption-desorption isotherms of nitrogen at 77 K with a BET analyzer (TRISTAR 3000 Micromeritics, U.S.), and the samples were out gassed at 180 °C in vacuum for 6 h.

The ORR was determined in 0.05 M Na_2SO_4 solution at pH = 3 (adjusted with 0.1 M H_2SO_4) using a Pine AFMSRXE 1523.40 mg G-GDE (or GDE) powder, and 10 mg acetylene black with 5 mL ethanol and 0.5 mL Nafion were mixed, grinding and ultrasonic oscillation was applied to yield a homogenous suspension ink. 50 μL mixture was dropped onto a glassy carbon disk electrode (geometric area of 0.196 cm^2) and then dried at room temperature for the rotating disk