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Fe-based metallic glass: An efficient and energy-saving electrode material for electrocatalytic degradation of water contaminants

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ABSTRACT

Excessive consumption of electrical energy has hampered the widespread application of electrochemical technology for degradation of various contaminants. In this paper, a Fe-based metallic glass (MG) was demonstrated as a new type of electrocatalyst to effectively and economically degrade an azo dye. In comparison to other typical electrodes, Fe-based MG electrodes exhibit a minimized degradation time, and the specific energy is 4–6 orders of magnitude lower than that of dimensionally stable anode (DSA), metal-like boron-doped diamond (BDD) and other electrodes. As sacrificial electrode materials, Fe-based MGs have less specific electrode mass consumption than iron electrodes. The use of Fe-based MGs will promote the practical application of electrochemical technology and the use of MGs as functional materials.

1. Introduction

Increasing pollution in water due to large-scale industrial production and extensive household waste generation poses a serious threat to the environment and human health. The release of azo dyes, for example, has attracted substantial public concern and presents a severe challenge for environmental scientists [1–3]. Among the various treatments for dyeing wastewater, electrochemical technology exhibits the best environmental compatibility because electrons are the main reagent in the process and are not contaminants. In addition, additional chemicals are not required in this process, reducing the possibility of secondary pollutants. The high efficiency, fast reaction rate and easy operation of electrochemical technology (ECT) make it very attractive for degradation of toxic organic pollutants [4–6].

An appropriate electrode material is critical for treating wastewater using ECT. Platinum is an excellent electrode material due to its good conductivity and chemical stability, even at high potentials and in very corrosive media. However, Pt is rarely used in practice because of its high cost. Many other cheaper electrodes, including iron, aluminum, stainless steel, graphite [7], metal-like boron-doped diamond (BDD) electrodes [8–10] and dimensionally stable anode (DSA) electrodes [11–16], have been developed for environmental remediation. However, these electrodes have pros and cons in treating wastewater, limiting their wide applications. For example, iron or aluminum anodes have been successfully used in electrocoagulation for degrading pollutants in various industrial wastewaters. However, their high energy consumption, large amounts of metal sludge production and short lifetime restrict their wide electrochemical treatment for environmental protection. BDD electrodes have high current efficiencies due to their strong resistance to deactivation *via* fouling, extreme electrochemical stability, no significant corrosion and a wide electrochemical potential window in aqueous solutions; while they require much more time for the electrochemical mineralization of organic compounds. DSA electrodes always require the irradiation of UV light during their usage, which is harmful to human beings. Thus, new electrode materials with optimum properties should be explored to promote the ECT for treating wastewater.

Metallic glasses (MGs) with long-range disordering and short-range ordering exhibit a good combination of desirable physicochemical properties, such as high strength, corrosion resistance, soft magnetic properties, and catalytic activity [17–21]. In the past few decades, MGs have attracted much attention as structural materials, but room temperature brittleness and high costs have restrained their further application. Very recently, Fe-based MGs was tested to degrade some azo dyes and showed a higher surface area-normalized degradation rate than crystalline Fe^0 and nano-

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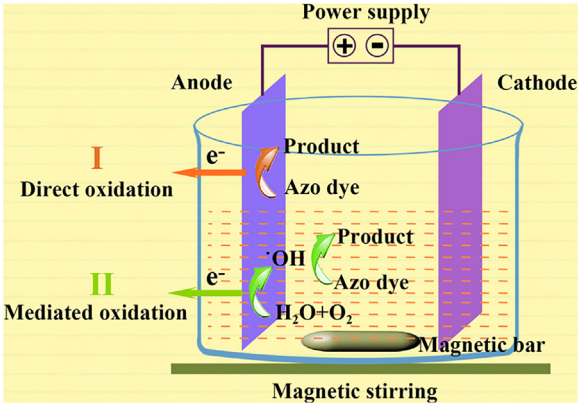

Fig. 1. Schematic illustration of electrochemical degradation of azo dyes using Fe-based MG electrodes.

Fe^0. More reactive sites due to the atomic structure of MGs have attributed to their superior ability to degrade azo dyes compared to their crystalline counterparts [22–25], which shows tremendous potential for the remediation of wastewater. Subsequently, some Mg-, MgZn-, Al- and Co-based MGs have been applied to degrade azo dyes in aqueous solutions [26–31]. Though all of these MGs exhibited ultrafast degradation rates, Fe- based MGs have attracted considerable attention because they are of low cost and easy to be recycled due to the soft magnetic property [32–38]. The degradation processes by Fe-based MGs have been accelerated by activating hydrogen peroxide or persulfate to produce high oxidative species, hydroxyl radicals ($^{\bullet}OH$) or sulfate radicals ($SO_4^{\bullet-}$). UV–vis light also demonstrates enhanced reaction rate [39–46]. However, the degradation efficiencies are sensitive to solution pH, concentration of hydrogen peroxide or persulfate, and irradiation intensity and it is difficult to control the reaction parameters. Until now, accelerating degradation rate and decreasing corrosion have been challenging with regard to their practical application.

In this work, we first report Fe-Si-B MG ribbons as electrodes for electrochemical treatment of azo dyes. A faster degradation rate was achieved. In addition, the Fe-Si-B MG ribbon electrodes were found to be superior to other electrode materials in reduced degradation time, improved degradation efficiency, and reduced energy consumption. These findings indicate that the developed technique combining MG and ECT (denoted as MG-ECT) results in significant improvements toward practical applications.

2. Experimental

Fe-based MG ribbons with a nominal composition of $Fe_{78}Si_9B_{13}$ (at.%) were prepared using a vacuum melt-spinning method. The ribbons were used without acid washing. Acid orange II (AO II, $C_{16}H_{11}N_2NaO_4S$, 350.3) was purchased from Sinopharm Chemical Reagent Co. Ltd, Shanghai, China without further purification. The AO II aqueous solutions (0.2–0.8 g L^{-1}) were prepared in 1 L by dissolving AO II at the desired concentration in distilled water. For a minimum conductivity of the solutions, sodium sulfate was added at a concentration of 0.25 M.

Electrochemical experiments were conducted in an open and cylindrical glass cell (500 mL) and performed at constant potential with positive and negative voltages alternately controlled by an electrochemical workstation (Fig. 1). The experiments were conducted at a constant temperature of 60 °C. In each run, an AO II solution (300 mL) was placed into a cylindrical glass cell. The Fe-based MG ribbons were used as both the anode and cathode. Ribbons with an approximate thickness of 25–30 μm were cut into pieces (3 cm × 13 cm) and subjected to electrochemical experiments. Before each run, both electrodes were weighed. The effective surface area of each electrode was 24.6 cm^2, and the electrode gap was 3 cm in all experiments. The cell voltage was adjusted to a desired value, and the electrochemical experiments were started. During the tests, the solution was stirred magnetically (200 rpm) to ensure homogenization and transport of the reactants towards/from the electrodes. At regular time intervals, a solution (3 mL) was withdrawn and used to measure the concentration of AO II after centrifugation for 5 min at 12000 rpm. The concentration of the AO II solution was analyzed using UV–vis spectroscopy (Purkinje General TU-1900, China) at a maximum wavelength of 484 nm, corresponding to the azo bond (—N=N—). Benzoic acid, a scavenger of hydroxyl radicals, was utilized to investigate the generation mechanism of the hydroxyl radicals. For comparison, iron foils served as the electrodes and were applied to electrochemically degrade AO II under the same experimental conditions. Chemical treatment of AO II was also conducted using the Fe-based MG ribbons under open circuit conditions without a current. All runs were repeated at least twice for statistical purposes. In addition, the Fe-based MG ribbons were reused to degrade dye without any treatment to study the stability of the Fe-based MG ribbons.

The structural features of the as-received Fe-based MG ribbons were studied using differential scanning calorimetry (DSC, Netzsch 204F1 and Netzsch 404C, Germany) with a heating rate of 20 K min^{-1} and X-ray diffraction (XRD, Rigaku D/max 2400, America). After the reaction, the Fe-based MG ribbons were washed thoroughly with ethanol to remove any solid residues on the surfaces, dried and reweighed, and then studied using DSC and XRD to examine the structural changes, and the surface morphology of the ribbons after reaction were also investigated using scanning electron microscopy (SEM, Zeiss SUPRA 55, Germany).

3. Results and discussion

3.1. Characterization of Fe-based MG ribbons

XRD pattern of the as-received ribbon exhibits a broad diffuse diffraction peak corresponding to an amorphous nature (Fig. 2(a)), which was further verified using DSC. Two obvious exothermic peaks in the range from 750 K to 850 K in the DSC curve (Fig. 2(b)) indicate the crystallization of the amorphous phase.

3.2. Fast degradation of AO II using MG-ECT

Fig. 3(a) shows the variation of UV–vis spectra for degradation of AO II using MG-ECT at a voltage of 1 V. The degradation of AO II using Fe-based MG ribbons without applying voltage is shown in Fig. 3(c). The characteristic absorption peaks of AO II at 230 nm and 310 nm and the shoulder peaks at 253 nm were attributed to the π–π* transitions related to the aromatic rings. The maximum absorption peak at 484 nm was ascribed to the n–π* transition of the azo bond (—N=N—) [47]. The peak height at 484 nm is proportional to the solution concentration. The ECT degradation process with a voltage of 1 V indicated that the absorption peak of the azo bond quickly faded out during the initial 10 min (Fig. 3(a)) and the solution rapidly became transparent (inset of Fig. 3(b)). After 10 min, only one absorption peak at 246 nm was observed, which corresponded to the amino groups (–NH_2) formed by the cleavage of the azo bond. In contrast, similar degradation of AO II took as long as 120 min for chemical degradation without a voltage, and the solution gradually became colorless (inset of Fig. 3(d)). These results intuitively imply that MG-ECT can significantly enhance the degradation capacity of AO II. The degradation efficiency (η) is defined as follows:

$$\eta = \left(1 - C_t/C_0\right) \quad (1)$$

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