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Preparation of Fenton-like coating catalyst on Q235 carbon steel by plasma electrolytic oxidation in silicate electrolyte

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ABSTRACT

Plasma electrolytic oxidation (PEO) on Q235 carbon steel has been applied in the silicate electrolyte. The ceramic coatings were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy, and scanning electron microscopy (SEM). The effects of ceramic coating preparation conditions on the surface morphology, composition, thickness and phenol degradation by Fenton-like reaction were investigated. The results indicated that the ceramic coating with porous structure was comprised of amorphous phases SiO_2 and Fe_3O_4. The average pore diameter and thickness of the ceramic coating increased slightly with the increase of reaction time and current density of PEO. In addition, the ceramic coatings were mainly composed of Si, Fe, Na, P, and O according to the EDS analysis. The phenol degradation experiments indicated that the removal efficiency was reduced with the increase of reaction time, but increased at 30 min. On the contrary, the degradation rate was first enlarged, and then decreased with the increase of current density. The 96% removal efficiency of phenol was achieved after 120 min degradation at the condition of 35 mg/L phenol, 6.0 mmol/L H_2O_2, pH 4.0 and $T = 303$ K while 6 cm^2 ceramic coating was used as Fenton-like catalyst which was prepared under 12 A/cm^2 and 10 min. The total leached Fe was below the EU directives (<2 mg/L). The leached Fe originated not only from the substrate, but also from ceramic coating. The unique advantages over the nanoparticle and excellent stability endowed it with desirable and promising application in the wastewater treatment.

1. Introduction

Recently, the development of green catalysts which can be efficiently separated for recycling after the reaction, has great significance for industrial application [1]. However, many traditional catalysts which exist in the form of powder need to be recycled through filtration or centrifugation which is time-consuming and inconvenient [2]. In order to overcome these issues, the coating catalysts presenting the advantages of easier recycling and reusability over powder catalysts, have achieved considerable attention in the field of water splitting [3], lithium battery [4], supercapacitor [5,6] and electro-Fenton [7], and so on. Motivated by their potential prospects, great efforts have been made to prepare coating catalysts such as chemical vapor deposition [8], sol-gel [9], hydrothermal method [10], atomic layer deposition [11], and anodic oxidation [12]. However, these methods have the drawbacks of high cost, time-consuming, weak adhesion strength and complex operation which have limited their large-scale commercial application.

Plasma electrolytic oxidation (PEO) as a cost effectiveness and environmental benign technique, is a promising surface modification technology, which has the properties of high adhesion, corrosion resistance, wear resistance, catalysis, thermal control and so on. Thus, it has been widely used to fabricate various functional ceramic coatings on the valve metals such as Mg, Al, Ti, etc. and their alloys [13–18]. However, there are only few published literatures about growing ceramic coatings on carbon steel by this method. Our group have prepared the low friction ceramic coating in silicate and sodium aluminate electrolytes [19,20]. Malinovschi, V. and his group synthesized anticorrosive aluminum oxide ceramic coating [21]. All of these coatings were fabricated for wear resistance and corrosion resistance application.

In this paper, the ceramic coatings on Q235 carbon steel prepared by PEO in silicate electrolyte were first applied in wastewater treatment as Fenton-like catalysts. The influences of reaction time and current density on surface morphology, composition and phenol degradation behavior by Fenton-like reaction were investigated. Fenton-like reaction develops from the Fenton reaction which utilizes Fe^{2+} as Fenton catalyst to decompose H_2O_2 for production of hydroxyl radicals with oxidation potential of 2.8 V to degrade the organic pollutant. However, Fenton-like reaction mainly makes use of solid catalyst containing iron

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as Fenton-like catalyst to generate hydroxyl radicals by decomposition of H_2O_2. Finally, the recyclability of the coating catalyst was also accomplished by four consecutive runs with almost no loss in catalytic activity, implying excellent stability of this material.

2. Experimental

2.1. Chemicals and materials

$Na_2SiO_3 \cdot 9H_2O$, $NaH_2PO_2 \cdot H_2O$, Phenol and NaOH were obtained from Sinoharm Chemical Reagent Co. Ltd., China. Hydrogen peroxide (analytical grade, 30%, w/w), H_2SO_4 were purchased from Xilong Chemical Co., Ltd. in China. All solutions used were prepared with deionized water.

2.2. Preparation of the ceramic coating in the silicate electrolyte

PEO technique was applied to fabricate the ceramic coating on the Q235 carbon steel in the silicate electrolyte. The rectangle Q235 carbon steel with a dimension of 20 mm × 20 mm × 0.5 mm, the composition of which was C 0.14–0.22%, Mn 0.30–0.65%, Si ≤ 0.30%, $P \leq 0.045\%$, S ≤ 0.05%, the rest Fe, wt.%. Before PEO, the Q235 carbon steel was polished with 500, 1000, 1500, 2000, 2500 mesh sand papers in sequence and then washed with deionized water, absolute alcohol and dried under ambient atmosphere. The homemade powder source with pulse peak current which was shown in Fig. 1, was used for plasma electrolytic oxidation of Q235 carbon steel. The silicate electrolyte contained 28 g/L $Na_2SiO_3 \cdot 9H_2O$ and 1.2 g/L $NaH_2PO_2 \cdot H_2O$. During PEO, the pretreated Q235 with 8 cm^2 was used as anode and stainless electrolyzer was served as cathode. The electric parameters and treatment time were shown in Table 1. In addition, average voltage-time curve during PEO process of $f = 2000$ Hz and $j = 12$ A/cm^2 was shown in Fig. 2. After the PEO, the ceramic coatings were taken out and washed with deionized water.

2.3. Analytic methods

The phase composition and surface morphology were characterized respectively by X-ray diffraction (XRD, Rigaku D/max-γB diffractometer, Cu Kα $\lambda = 0.15406$ nm radiation) and scanning electron microscopy (SEM, FEI Quanta 200). Surface composition of the sample was analyzed by X-ray photoelectron spectroscopy (XPS, PHI 5400 ESCA System, Mg Kα radiation). The phenol concentration was determined by 4-aminoantipyrine method on a UV/Vis spectrophotometer (Lambda XLS, PerkinElmer). The concentration of total iron in the bulk solution leached from the catalyst was evaluated by 1,10-phenanothroline method.

Table 1
The electric parameters of PEO process and treatment time.

J^a (A/cm^2)	t^b (min)	f^c (Hz)
12	10	2000
12	15	2000
12	20	2000
12	30	2000
15	15	2000
18.75	15	2000

[a] j represented current density.
[b] t was treatment time.
[c] f was the short name of frequency.

2.4. Phenol degradation experiments

The phenol degradation experiment was carried out in a 100 mL beaker containing 50 mL 35 mg/L phenol under the magnetic stirring at 400 rpm at 303 K. Before degradation, the phenol solution was adjusted to pH 4.0 by adding 0.1 mol/L H_2SO_4. And then, the ceramic coatings with a geometry area of 6 cm^2 prepared under different conditions were immersed into phenol solution. Finally, the degradation reaction was initiated, once hydrogen peroxide solution (0.34 mL, 3 wt.%) was added. During phenol degradation, 0.25 mL samples were removed with a pipette at a given time for absorbance measurement with UV/Vis spectrophotometer. The experiments were carried out in triplicates and average values and standard deviations were shown below.

3. Results and discussion

3.1. Surface morphology, elemental analysis and thickness of the ceramic coating catalysts

The development of surface morphology, the coating thickness and element content of PEO ceramic coatings prepared under different reaction time and current density was illustrated in Figs. 3, 4 and Table 2. The surface of the coatings was porous and rough due to plasma

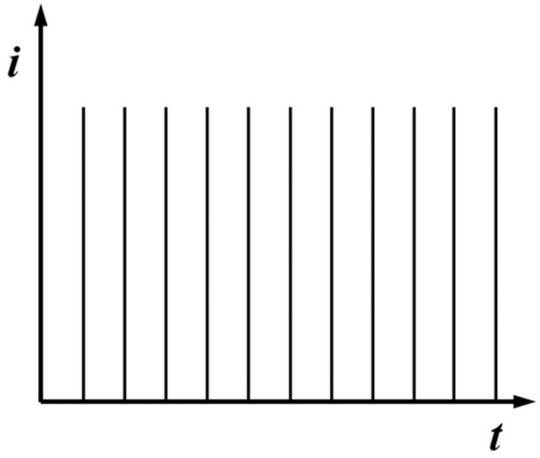

Fig. 1. Current waveform of PEO power source.

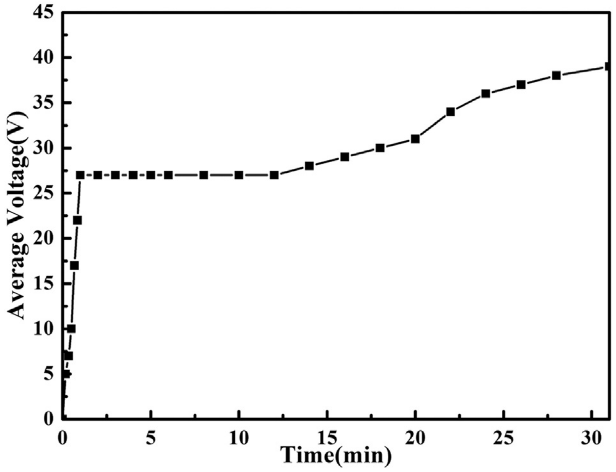

Fig. 2. The average voltage evolution plots during PEO process of $f = 2000$ Hz and $j = 12$ A/cm^2.

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