



Electrochemical treatment of artificial humidity condensate by large-scale boron doped diamond electrode



Hao Li^a, Qingni Yu^{a,b}, Bin Yang^{a,*}, Zhongjian Li^a, Lecheng Lei^a

^a Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

^b National Key Laboratory of Human Factors Engineering, China Astronaut Research and Training Center, Beijing 100094, China

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ABSTRACT

Electrochemical treatment of artificial humidity condensate (AHC) in confined space has been conducted. Large-scale boron-doped diamond (BDD) film was deposited on Ta substrate by hot filament chemical vapor deposition, and its uniformity was evaluated by the Raman shift intensities on the basis of statistical analysis. BDD electrode was used as anode for the oxidation of organic compounds, and almost 98% final TOC removal efficiency of AHC was achieved. Higher oxidation rate constant, higher initial instantaneous current efficiency and lower specific energy consumption were obtained for the larger surface area electrode. Based on the detection of intermediates by HPLC and IC, a possible degradation pathway of AHC was also proposed. In addition, the potential utilization of H₂ generated on cathode for fuel cell was discussed. It is estimated that about 5% electric energy can be offset the electrochemical treatment cell by using the integrated operation.

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1. Introduction

Humidity condensate (HC) is generated from the condensation of water vapor owing to the variation of temperature and humidity when human beings live in confined space for a long time such as space station or submarine, and it consists of a little amount of small molecule alcohols, acids and inorganic salts [1]. It is the most realistic and economical way to treat it for the supplement of drinking water because of its relatively clean quality [2]. Sorption-catalytic oxidation of HC was employed with high efficiency, where Pt was used as the catalyst and oxygen as the oxidizer [3,4]. However, the method suffered from high consumption of adsorbents and energy, and the operating cost was high. Due to the limitation of space, localized treatment facilities should be compact and easy to install and operate. Herein, electrochemical technology offers an alternative solution, because electrons provide a versatile, efficient, cost-effective, and clean reagent for the decontamination of wastewater, and the facility is easily automated [5].

Anode is considered as the most important part on affecting the performance of electro-catalytic oxidation, because it governs the yield of generated oxidants (i.e. ·OH) [6]. Some drawbacks of common anodes were reviewed by Chen [7]. It was addressed that glassy carbon anode induced a rapid loss of activity, PbO₂ would

release toxic ions, SnO₂ had a limited service life, and IrO₂ had an incomplete or inefficient oxidation. Recently, boron-doped diamond (BDD) electrode has been attracted great attentions, especially for its particular properties including the wide potential window, low background current, high electrochemical stability and corrosion resistance [7–9]. BDD electrodes had been widely used as anodes for the degradation of refractory organic pollutants, such as nitrobenzene [10], salicylic acid [11], real textile effluent [12], dyestuff [13], perfluorinated compounds [14], sulfachloropyridazine [15], sulfanilic acid [16], methyl orange azo dye [17], real landfill leachate [18], and chlorophenoxy herbicides [19]. Meanwhile, reduction reaction simultaneously occurs at the cathode, resulting in generation of H₂. Jiang and coworkers demonstrated that the H₂ evolution rate in the system equipped with BDD electrode was significantly increased in comparison with Pt electrode because of widening of the potential window and proposed the utilization of H₂ for fuel cell operation [20].

BDD thin film was usually deposited on the substrates as electrodes such as Si, Ti, Nb and Ta. The material of Ta can be utilized as a better candidate for the fabrication of large-scale BDD electrode, because it possesses excellent mechanical strength, high electrical conductivity and good chemical stability [21]. The thermal expansion coefficient of Ta ($6.3 \times 10^{-6} \text{ K}^{-1}$) is closer to that of diamond ($1.0 \times 10^{-6} \text{ K}^{-1}$). The lower difference of thermal expansion between the deposited film and substrate would benefit the mutual adhesion during the temperature-falling period in the fabrication procedure. Zhang and coworkers fabricated a Ta/BDD

* Corresponding author. Tel./fax: +86 571 87952525.

E-mail address: keyangb@zju.edu.cn (B. Yang).

electrode with the diameter of 1.27 cm for anodic oxidation of salicylic acid [22]. Their results showed that Ta/BDD exhibited high electro-catalytic activity for the degradation of organic compounds and chemical oxygen demand was reduced from 830 mg L⁻¹ to 42 mg L⁻¹ under the current density of 200 A m⁻² at 30 °C. However, the relatively small size of Ta/BDD cannot fulfill the large-scale requirements in industrial applications.

Therefore, it is essential to scale up the electrode area in order that the treatment capacities can be increased and the facility will be more compact. In the present study, the large-scale BDD film deposited on Ta substrate up to 150 mm was fabricated using hot filament chemical vapor deposition (HFCVD) method. The BDD film uniformity were investigated by the statistical analysis on the Raman shifts and their intensities. Then the BDD electrodes were employed to degrade the artificial humidity condensate (AHC). The effects of the operating parameters including electrode area, applied current density, and electrode gap on the reaction rate and mineralization efficiency were systematically investigated. The current and energy efficiencies of electro-catalytic oxidation were also evaluated, especially for the increased electrode area. The oxidized by-products including organic products and inorganic ions were determined by high-performance liquid chromatography (HPLC) and ion chromatography (IC), respectively. A possible oxidative degradation pathway of AHC was proposed and clarified. Moreover, the potential utilization of H₂ were discussed since it is inevitable produced during electrolysis.

2. Experimental

2.1. Preparation of BDD electrode

BDD films were synthesized on a Ta disc with the thickness of 0.1 cm using HFCVD technique, and the diameter ranged from 75 mm to 150 mm (the corresponding area ranged from 44.2 cm² to 176.7 cm²). Prior to the deposition, the Ta surface was firstly pretreated by sandblasting, and then seeded by ultrasonically rubbing for 60 min in an acetone suspension with 1 μm sized diamond paste (Kemet, England). The reactive gas used was 2% methane in H₂, and 60 ppm of diborane was added as the boron dopant. The gas mixtures were supplied to the deposition chamber at the flow rate of 500 sccm and the pressure of the chamber was maintained at 5 kPa. The schematic diagram of the deposition process is shown in Fig. 1. The gas mixture was well dispersed over the Ta substrate through the discharge from tiny needle holes, which were located in the inner circle of the gas inlet ring. The Ta substrate was placed on the Cu platform, where the rotation rate was set at 2 rpm. The substrate temperature was controlled by the water chiller, and

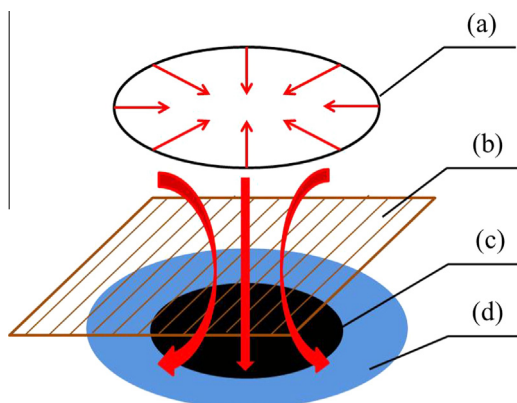


Fig. 1. The schematic diagram of deposition process: (a) gas inlet ring, (b) filament, (c) Ta substrate, (d) Cu platform.

the pipe of cool water was connected with the Cu platform. During the deposition stage, the temperature of the filament and the substrate were set at about 2500 °C and 800 °C, respectively. The deposition time was set for 15 h.

2.2. Characterization of BDD films

The morphologies of BDD films were characterized by means of scanning electron microscope (SEM, Hitachi SU-70, Japan). The crystalline microstructures of the film were analyzed by X-ray diffraction (XRD, Shimadzu XRD-6000, Japan) and UV laser Raman spectroscopy (LabRamHRUV, JDbio-yvon, France). Since the area of BDD film was large, nine symmetric points on the surface of the film were chosen for Raman analysis and the uniformity was evaluated by the statistical method.

2.3. Artificial humidity condensate

Chemicals in analytical grade used for degradation experiments were purchased from Aladdin Industrial Inc. China. All solutions were prepared with ultra-pure water at room temperature. On the basis of the literatures [23,24], the main compositions and corresponding concentrations in AHC are recommended and summarized in Table 1.

2.4. Electro-catalytic oxidation of AHC

200 mL AHC was treated in a one-compartment and thermostatic cylindrical cell by galvanostatic electrolysis. The BDD film was arranged as anode while the same area stainless plate was used as cathode. The AHC solution was introduced in a reservoir and then continuously circulated with a peristaltic pump at the flow rate of 1.45 mL s⁻¹. The thermostat water bath was used to keep the solution at 25 °C. The diameter of electrodes varied from 75 to 150 mm, and the current ranged from 0.21 to 1.06 A.

2.5. Determination of intermediates

Mineralization of AHC was monitored by the abatement of TOC values, and TOC was analyzed with a TOC V-CPH analyzer (Shimadzu Corporation, Japan). The concentrations of specific organic compounds in AHC and corresponding intermediates were identified by HPLC (Agilent 1200) equipped with a UV-Visible detector and an Eclipse XDB C18 (3.5 μm, 4.6 mm × 150 mm) column. The mobile phase was composed of 0.02 mol L⁻¹ KH₂PO₄ solution and methanol with the ratio of 93/7 (v/v) at the flow rate of 1 mL min⁻¹, where the pH of KH₂PO₄ solution was adjusted to 2.5 by using H₃PO₄. The detection wavelength was set at 210 nm. Inorganic ions in solution were identified by IC (Dionex ICS 1100) fitted with a AS18 or AS16 (4 mm × 250 mm) column at the temperature of 35 °C. The mobile phase was 0.023 mol L⁻¹ KOH solution at the rate of 1 mL min⁻¹. H₂ gas was measured by gas chromatography (FULI 9790-TCD).

The TOC removal efficiency, η (%), was calculated from Eq. (1).

$$\eta = \frac{\text{TOC}_0 - \text{TOC}_t}{\text{TOC}_0} \times 100\% \quad (1)$$

where TOC_0 and TOC_t are the solution TOC values before electrolysis and at time t (mg L⁻¹). The instantaneous current efficiency (ICE) based on TOC value was calculated from Eq. (2).

$$\text{ICE} = FV \frac{\text{TOC}_t - \text{TOC}_{t+\Delta t}}{8I\Delta t} \quad (2)$$

where TOC_t and $\text{TOC}_{t+\Delta t}$ are the solution TOC values at time t and $t + \Delta t$, respectively (mg L⁻¹), V is the solution volume (L), F is Faraday constant (96,485 C mol⁻¹), and I is the applied current

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