

Comparative study of oxidation ability between boron-doped diamond (BDD) and lead oxide (PbO₂) electrodes

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Abstract: The electrochemical oxidation capabilities of two high-performance electrodes, the boron-doped diamond film on Ti (Ti/BDD) and the lead oxide film on Ti (Ti/PbO₂), were discussed. Hydroxyl radicals ($\cdot\text{HO}$) generated on the electrode surface were detected by using *p*-nitrosodimethylaniline (RNO) as the trapping reagent. Electrochemical oxidation measurements, including the chemical oxygen demand (COD) removal and the current efficiency (CE), were carried out *via* the degradation of *p*-nitrophenol (PNP) under the galvanostatic condition. The results indicate that an indirect reaction, which is attributed to free hydroxyl radicals with high activation, conducts on the Ti/BDD electrode, while the absorbed hydroxyl radicals generated at the Ti/PbO₂ surface results in low degradation efficiency. Due to quick mineralization which combusts PNP to CO₂ and H₂O absolutely by the active hydroxyl radical directly, the CE obtained on the Ti/BDD electrode is much higher than that on the Ti/PbO₂ electrode, notwithstanding the number of hydroxyl radicals produced on PbO₂ is higher than that on the BDD surface.

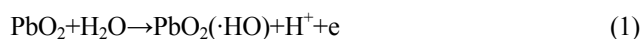
Keywords: thin films; diamond films; lead oxide; born doping; hydroxyl radicals; chemical oxygen demand (COD); oxidation

1. Introduction

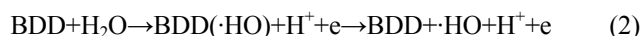
Electrochemistry is believed to be one of the most promising approaches for wastewater treatment, especially when the water contains biorefractory pollutants [1–2]. It aims to degrade organic contaminants to biodegradable products or mineralize them to CO₂ and H₂O directly. However, it is not used widely due to the short service-life of electrodes that is attributed to the fouling and passivation effects of anodes, high energy consumption, and high cost. The electrochemical oxidation performance strongly relies on the electrode (mainly the anode). In the past several decades, people have employed many electrodes, such as the metal, carbon electrode, and dimension stabled anode (DSA), to improve the electrochemical incineration properties and reduce energy consumption.

Recently, many researches have been carried out to assess high-performance electrodes like the boron-doped diamond film on Ti (Ti/BDD) [3] and the lead oxide film on Ti

(Ti/PbO₂) [4], which have received great attention for the anodic oxidation of toxic and biological refractory pollutants. Ti/BDD and Ti/PbO₂ have been classified as “nonactive anodes” [5], and hydroxyl radicals ($\cdot\text{HO}$) from the decomposition of H₂O on the surfaces of two electrodes can interact with the organic compound instantly. However, the generated hydroxyl radicals have different types on the surfaces of two electrodes. On the PbO₂ surface, anodic discharge of water at the active site produces absorbed hydroxyl radicals (PbO₂($\cdot\text{HO}$)), which will be restricted on the surface due to the porous structure of PbO₂ [6]. The reaction can be shown as



With the weak surface absorption property, large part of absorbed hydroxyl radicals disengage from the BDD surface and become free hydroxyl radicals ($\cdot\text{HO}$) as the following equation shown:



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The free hydroxyl radicals consequently react with the organic compound and degrade the pollutant completely. Furthermore, due to the weak $\cdot\text{HO}$ absorption, the anode does not participate in the side reaction (O_2 evolution). The decomposition of $\cdot\text{HO}$ is prolonged. As a result, Ti/BDD has a very lower activity for O_2 evolution and a higher current efficiency than the Ti/ PbO_2 electrode. The anode potential on BDD can be up to 2.8 V vs. the standard hydrogen electrode (SHE) [7]. It is about 1 V higher than the PbO_2 electrode [8].

Furthermore, the short service-time and the potential contamination of toxic lead restrict the large-scale application of PbO_2 electrodes. While, as aforementioned, BDD has high stability and high performance in almost all solutions, even in strong aggressive media. The lifetime of the Ti/BDD electrode measured by the acceleration time test is more than 570 h, which is quite larger than that of the Ti/ PbO_2 electrode. The aforementioned results demonstrate that the Ti/BDD electrode is more efficient and stable than the Ti/ PbO_2 electrode.

The electrogeneration capabilities of hydroxyl radicals on Ti/BDD and Ti/ PbO_2 electrodes were discussed by using *p*-nitrosodimethylaniline (RNO) as the trapping reagent in this work. The wastewater containing *p*-nitrophenol (PNP) widely used in many chemical plants was chosen as the model substrate in the bulk electrolysis measurement, which is rough to deal with and has been classified as a priority pollutant by the United States Environmental Protection Agency (EPA) [9]. The aim was to describe the abatement mechanism of hydroxyl radicals generated by Ti/BDD and Ti/ PbO_2 via comparing the results of electrolysis of RNO and PNP on these two electrodes. Furthermore, the current efficiency was investigated and assessed briefly.

2. Experimental

2.1. Preparation and characterization of the electrodes

The Ti/BDD electrode was prepared by boron-doped diamond film deposition on the Ti substrate using a microwave plasma-assisted chemical vapor deposition (MPCVD) system with the output frequency of 2.45 GHz. The reactant gas was a mixture of H_2 and CH_4 . B_2H_6 diluted by H_2 to 2vol% was used as the boron source. The Ti/ PbO_2 electrode was made by electrochemical oxidation of an aqueous solution of lead nitrate on the Ti plate [10].

The surface morphology and microstructural details were characterized by scanning electron microscopy (SEM,

LEO-1450) and micro-Raman spectroscopy (JY-H2800, 532 nm, 3 mW). The service life of the Ti/BDD electrode was shown to be over 570 h in an accelerated life test (3 mol H_2SO_4 at a current density of $10^4 \text{ A}\cdot\text{m}^{-2}$), which was longer than that of the Ti/ PbO_2 electrode (less than 100 h in 3 mol H_2SO_4 at a current density of $500 \text{ A}\cdot\text{m}^{-2}$).

2.2. Electrolysis system

Bulk electrochemical oxidations were carried out in a one-compartment cell under galvanostatic condition at room temperature. The prepared Ti/BDD and Ti/ PbO_2 electrodes were used as the anode with an area of 4 cm^2 , respectively. The cathode was a stainless steel sheet with the same area. The interelectrode distance was 1 cm. The solutions of RNO and PNP were conducted to the cell, respectively.

2.3. Analysis

Following the bleaching of RNO solutions, the electro-generation of $\cdot\text{HO}$ intermediates was monitored. RNO can be traced at 440 nm using a UV-vis spectrophotometer (Specord 200, Analytikjena).

The chemical oxygen demand (COD) of the solutions was monitored by a titrimetric method using dichromate as the oxidant in acidic solution. The current efficiency (CE) was calculated from the value of COD using the following equation [11]:

$$\text{CE} = \frac{\text{COD}_t - \text{COD}_{t+\Delta t}}{8I\Delta t} FV \quad (3)$$

where COD_t and $\text{COD}_{t+\Delta t}$ are the chemical oxygen demands at time t and $t+\Delta t$, respectively, $\text{g}\cdot\text{dm}^{-3}$; I is the current, A; F the Faraday constant, $96487 \text{ C}\cdot\text{mol}^{-1}$; and V the volume of the electrolyte, dm^3 .

3. Results and discussion

3.1. Morphology and crystal structure of the electrodes

The microstructure of the Ti/BDD surface is shown in Fig. 1. It can be observed that the boron-doped diamond film displays a very compact crystalline structure. It presents a typical pyramid facets and (111) orientation. The average crystal size of BDD is less than $1 \mu\text{m}$. The small crystal size provides high surface area and more active sites where electrochemical reactions are carried out [3]. The compact film can prevent the substrate from corrosion, and the high film quality can show superior electrochemical properties [12].

Fig. 2 shows the Raman spectrum of the BDD film. One

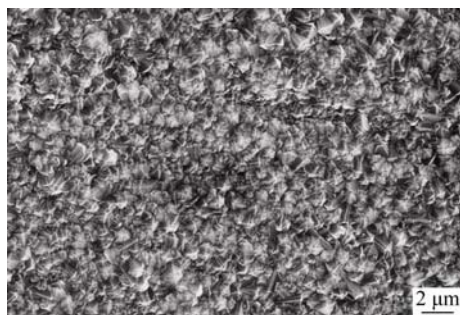


Fig. 1. SEM micrograph of the boron-doped diamond film on the Ti substrate (Ti/BDD).

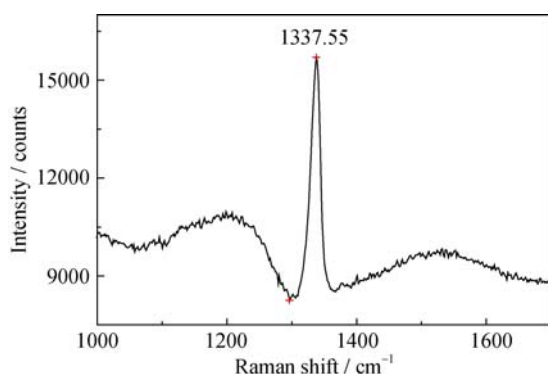


Fig. 2. Raman spectrum of the boron-doped diamond film on the Ti substrate (Ti/BDD).

sharp peak at 1337.55 cm^{-1} due to the sp^3 C–C bond can be observed. The result implies that a high quality diamond film is deposited on the titanium sheet. However, compared with the Raman shift of instinct diamond (1332.5 cm^{-1}), this peak of the doped film has a shift of 5 cm^{-1} , and the intensity of the peak becomes weaker. The peak shift to higher wave numbers is due to the residual compressive stress [13]. Furthermore, two obvious wide peaks appear around 1220 and 1500 cm^{-1} , which are originated from the Fano interaction [14] and the appearance of graphite, respectively. The conclusion is consistent with many other authors [15–16].

3.2. Detection of hydroxyl radicals

Because of the rapid reaction between RNO and $\cdot\text{HO}$, RNO can be used as the trapper to detect the generation of hydroxyl radicals on the electrodes, where $\cdot\text{HO}$ consists of not only the free hydroxyl radicals but also the absorbed hydroxyl radicals.

Fig. 3 shows the RNO removal evolution of these two anodes. Compared with the Ti/BDD electrode, Ti/PbO₂ shows a higher capability in degrading RNO. After 30 min, the RNO removal for the Ti/PbO₂ anode is over 98%, while about 76% for the Ti/BDD anode. It demonstrates that the Ti/PbO₂ electrode has a stronger generation capacity of $\cdot\text{HO}$

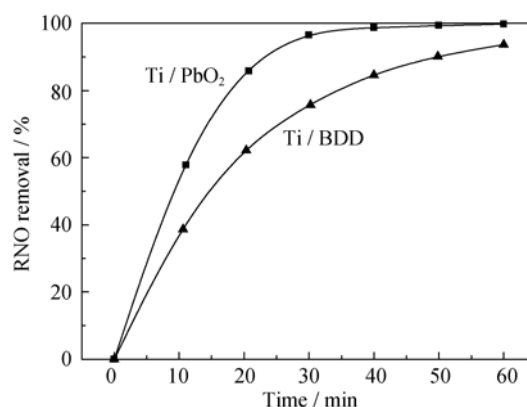
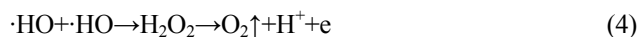


Fig. 3. Relationship between the RNO removal and time using Ti/BDD and Ti/PbO₂ anodes during electrolysis of $2 \times 10^{-5}\text{ mol}\cdot\text{L}^{-1}$ RNO.

radicals than the Ti/BDD electrode.

As mentioned by Chen [17], because of the stronger capacity of absorption, the intermediates produced by water discharge on the surface of PbO₂ anodes mainly exist as the type of absorption. Significant quantities of hydrogen peroxide are expected to be formed by combining the absorbed hydroxyl radicals with each other. Afterward, further anodic oxidation to oxygen (side reaction) may occur as shown in the following equation, which can be confirmed by the relative low oxygen potential (1.75 V in $1\text{ mol H}_2\text{SO}_4$).



However, diamond has a weak absorption capability, resulting in generating more free hydroxyl radicals which will diffuse into the electrolyte. These hydroxyl radicals are hard to combine with each other and have strong mineralization ability [18].

3.3. Degradation assays of PNP

The COD removal as a function of electrical charge is shown in Fig. 4, where the solution is adjusted by $1\text{ mM PNP} + 0.2\text{ M Na}_2\text{SO}_4$ and the current density is kept at $20\text{ mA}\cdot\text{cm}^{-2}$ at room temperature. The curves demonstrate that the Ti/BDD electrode has a greater capacity of oxidizing PNP than the Ti/PbO₂ electrode. The COD removal is almost 100% on the Ti/BDD electrode when the applied electrical charge is $3.2\text{ A}\cdot\text{h}\cdot\text{L}^{-1}$, and it is less than 50% on the Ti/PbO₂ electrode under the same test condition.

For the nonactive electrode, the reaction mechanism is defined as the indirect electrochemical oxidation mediated by hydroxyl radicals [5]. However, PbO₂ has a stronger capacity of $\cdot\text{HO}$ generation but a weaker ability of COD abatement than the BDD electrode. The above results confirm the judgment that hydroxyl radicals produced by BDD

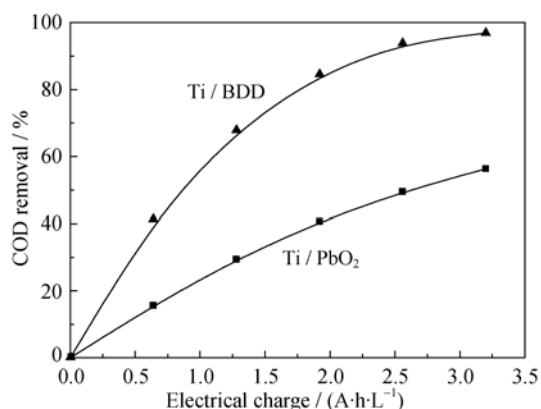


Fig. 4. Relationship between the COD removal and electrical charge on Ti/BDD and Ti/PbO₂ electrodes in the solution of 1 mM PNP+0.2 M Na₂SO₄.

mainly exist in the free type, which has a stronger mineralization capability than the absorbed hydroxyl radicals generated by the PbO₂ electrode. On the other hand, the amount of ·HO generated by BDD is more efficient to destroy PNP and/or intermediates to CO₂ and H₂O, which results in the 100% COD removal in a short time. While more absorbed ·HO produced on the PbO₂ surface reacts with each other and/or more intermediates are generated on the PbO₂ electrode than on the Ti/BDD electrode [19].

3.4. Current efficiency (CE)

Fig. 5 shows the current efficiency of these two electrodes. Obviously, Ti/BDD is much more effective than Ti/PbO₂ in the degradation of PNP, but the CE value is relatively low in the study. High CE is not only attributed to the difficulty of O₂ evolution but also related to the limiting current estimated from the COD value as [20]:

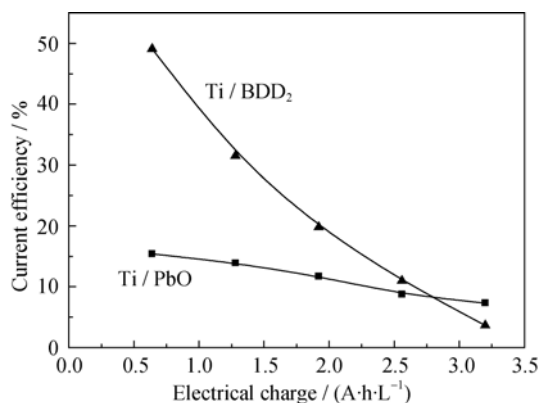


Fig. 5. Relationship between current efficiency and electrical charge on Ti/BDD and Ti/PbO₂ electrodes.

$$i_{\text{lim}}(t) = 4Fk_m \text{COD}(t) \quad (5)$$

where i_{lim} is the limiting current density at a given time t ,

$A \cdot m^{-2}$; F the Faraday's constant, $C \cdot mol^{-1}$; k_m the average mass transport coefficient in the electrochemical reactor, $m \cdot s^{-1}$; $\text{COD}(t)$ is the chemical oxygen demand at a given time t , $mol \cdot m^{-3}$; and 4 the number of exchanged electrons per mol of O₂.

When the applied current density $i < i_{\text{lim}}$, the instantaneous current efficiency (ICE) is 100%, and COD decreases linearly with time. The electrolysis is under current control. While the applied current density $i > i_{\text{lim}}$, the ICE is less than 100%, and the COD removal follows an exponential trend. According to the estimation, the applied current density is larger than i_{lim} all the time; the electrolysis is under mass transport control.

For the Ti/BDD electrode, many hydroxyl radicals were generated on the surface by the discharge of water and then transferred to the vicinity of the electrode, and reacted with the pollutants. Under the condition of mass transport control, no sufficient PNP could be transferred quickly to the ambient of generated ·HO and participated in the degradation reaction immediately. Therefore, parts of free hydroxyl radicals had to combine with each other to form O₂ (side reaction), which resulted in a degeneration of CE quickly. For the Ti/PbO₂ electrode, the absorbed hydroxyl radicals existed on the electrode surface have weaker activation in the degradation of PNP than the free ·HO generated by the Ti/BDD electrode. Therefore, a large mass of absorbed hydroxyl radicals evolved to O₂ by the side reaction competing with the reaction of pollutant mineralization simultaneously. In the condition of mass control, although a softly descent curve of CE was obtained on the Ti/PbO₂ electrode in the study, the CE value on the Ti/PbO₂ electrode was much lower than that of Ti/BDD. It is suggested that Ti/BDD has more effective energy consumption than Ti/PbO₂. If the applied current density remains below the limiting current density (i_{lim}), 100% current efficiency will be obtained probably.

4. Conclusions

(1) Both Ti/BDD and Ti/PbO₂ electrodes have evident abilities to produce ·HO intermediates. It is obvious that Ti/PbO₂ has a stronger capability of hydroxyl radical generation compared to the Ti/BDD electrode.

(2) However, Ti/PbO₂ has a weaker oxidation ability in COD removal than the Ti/BDD electrode. This phenomenon results from the different types of generated hydroxyl radicals. Due to the weak absorption of BDD, hydroxyl radicals generated on the Ti/BDD electrode exist as the free type ·HO.

While on the Ti/PbO₂ anode surface, the generated ·HO mainly exist as the adsorbent type and is easy to combine with each other.

(3) The CE on the Ti/BDD electrode is much higher than that on the Ti/PbO₂ electrode due to the rapid reaction between free ·HO and the pollutants. However, due to the fact that the applied current density is higher than the limiting current density, the CE is not high enough even for the Ti/BDD electrode.

(4) It can be concluded that if a lower current density is applied, a higher CE even up to 100% can be obtained on the Ti/BDD electrode. It is demonstrated that Ti/BDD is a promising material in wastewater treatment, attributing to the stronger capacity of free ·HO generation and the ideal energy consumption when the conduction can be optimized.

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