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Typical Rare Earth Doped Lead Dioxide Electrode: Preparation and Application

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Typical rare earth doped lead dioxide electrode (Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2) was prepared by the thermal decomposition electrodeposition technique for the treatment of simulated wastewater containing *p*-toluene sulfonic acid (*p*-TSA). Under the conditions of initial quality concentration of *p*-TSA 500mg·L^{-1}, current density 30mA·cm^{-2}, pH 2 and room temperature, after 3 hours degradation, the removal rates of *p*-TSA, COD and TOC arrived 96.05%, 59.40% and 38.00% for Ti/Sb-SnO_2/PTFE-La-β-PbO_2. The results showed that the rare earth doped electrode could cover the advantages both catalytic efficiency and stability. What's more, based on the electrode structure analysis of XRD and SEM, the modified mechanism of La doped was also proposed, which would be helpful for rare earth application in wastewater pollution control.

Keywords: electrocatalysis; typical rare earth doped lead dioxide electrode; *p*-toluene sulfonic acid; La

1. INTRODUCTION

Highly concentrated pharmaceutical wastewater was a challenge of environmental concern for the large emission, the high concentration of organic and the poor biodegradability. Traditional treatment technologies, such as biological, physical and chemical treatment could not meet the demand of increasingly strict discharge standard. Therefore, alternative way, including ozonation oxidation [1], photochemical [2] and peroxide/UV [3] treatment, etc, had been researched for the pharmaceutical wastewater treatment was an urgent demand for the environmental workers and the government [4-6]. The choice of treatment also depends on economics as well as ease of control, reliability and efficiency of the treatment.

Electrochemical oxidation technology, which characterized by stable high efficiency and environmental friendly process, had been applied among many different fields of environmental pollution treatments [7-9]. Numerous electrode materials could be used to oxidize organic wastes. But, in traditional electrochemical oxidation system, especially for the degradation of high concentration organic wastewater, oxidation or reduction on electrode surface would produce a polymer film, which resulted in low electrode activity and high power consumption [10, 11]. Therefore, the electrode materials and the electrolysis conditions should to be improved, for high effective and economical degradation. Electrode was known as the “core” of electrochemical oxidation system. Therefore, BDD and various metal oxides film electrodes, e.g., PbO_2, SnO_2 and RuO_2 had been studied [12-14]. Since the discovery of dimensionally stable anodes (DSA) nearly 30 years ago [15], there had been a successful development about DSA electrode, and much researches had also been done on finding and preparing new DSA anodes for high stability, high activity and low cost of electrodes. Among them, PbO_2 electrode was treated as an excellent one owing to its lower price, chemical stability and high overpotential for the oxygen evolution reaction. What’s more, PbO_2 anode could also be electrogenerated both in acidic [16, 17] and alkaline solutions containing Pb^{2+} ions [18]. The electrodeposition process mainly involved the following stages [17]:

$$H_2O \rightarrow OH_{ads} + H^+ + e^- \quad (1)$$

$$Pb^{2+} + OH_{ads} \rightarrow Pb(OH)^{2+} \quad (2)$$

$$Pb(OH)^{2+} + H_2O \rightarrow PbO_2 + 3H^+ + e^- \quad (3)$$

In this work, considering the rare earth with special 4f electronic structure [7, 19, 20], a typical rare earth doped lead dioxide electrode prepared by thermal decomposition electrodeposition technique was used for the treatment of simulated wastewater containing *p*-toluene sulfonic acid (*p*-TSA). Different doped moral ratios of rare earth had also been discussed for the optimal one. Chemical oxygen demand (COD) and total organic carbon (TOC) were tested to value the degradation efficiency of the Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 electrode. Finally, based on the results of scanning electron microscope (SEM) and X-ray diffraction (XRD), the modified mechanism of La doped was proposed, which would be helpful for rare earth application in wastewater pollution control.

2. MATERIALS & METHODS

2.1 Materials

All regents were of analytical reagent grade. The thickness of Ti sheets was 1mm. All solutions were prepared with deionized water.

2.2 The structure of electrode

The typical rare earth doped lead dioxide electrode (Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2) was composed by four layer (Ti substrate, SnO_2+Sb_2O_3 layer, α-PbO_2 layer and PTFE-La-β-PbO_2 layer). The profile chart of electrode was shown as Fig.1.

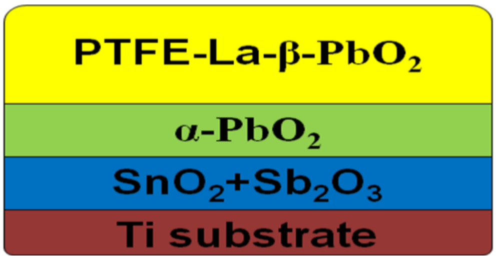

Figure 1. The profile chart of Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 electrode

2.3 Preparation of electrodes

Ti/SnO_2-Sb_2O_3 electrodes, which were prepared through the thermal decomposition method, were used as the substrates for the electrodeposition of PbO_2 films. And, the PbO_2 films were composed by α-PbO_2 layer and β-PbO_2 layer. The electrodeposition of α-PbO_2 layer was prepared by the electrolyte contained 4~5 mol·L^{-1} NaOH and 0.1 mol·L^{-1} PbO, and performed with a current density of 4~5 mA·cm^{-2} for 60 min at a temperature of 60 ºC. Then, the electrolyte for electrodeposition of β-PbO_2 was composed of 0.4~0.6 mol·L^{-1} $Pb(NO_3)_2$, 0.1~0.2 mol·L^{-1} KF·$2H_2O$, 4mL·L^{-1} polytetrafluororethlene (PTFE 60wt%), and the pH was adjusted to 1.68 with HNO_3. Rare earth oxides (lanthanum oxide, La_2O_3), were added into the solution and dispersed in an ultrasonic bath for 15 min before electrodeposition, which plated under the current density of 4~5 mA·cm^{-2} for 120 min at a temperature of 80 ℃. Finally, Ti/SnO_2-Sb_2O_3/PTFE-β-PbO_2 and Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 electrodes were rinsed with deionized water.

2.4 Methods

In this study, the samples were selected depending on the time duration of 0, 30, 60, 90, 120, 150 and 180min. The concentration of *p*-TSA was measured by a High performance liquid chromatography system (1200HPLC, Agilent Technologies, USA), equipped with an RP-C18 column (4.6mm×150mm). The mobile phase was mixture of 0.015% (V%) trifluoroacetic acid and methanol (70:30, v/v). Flow rate was set at 0.8ml min^{-1}. Injection volume was 5µl, and the column temperature was 30 ºC. The UV detector was set at 230nm. The chemical oxygen demands (COD) was determined by the dichromate method (HJ/T339-2007), and the detection wavelength was 440nm. The total organic carbon (TOC) was examined using the TOC analyzer (TOC-V CPN, SHIMADZU, Japan). The surface morphology of the coatings was examined by SEM (Hitachi5570, Hitachi, Japan). An X-ray diffractometer (X'Pert PRO, PNAlytical, Netherlands) was used to analyze the crystalline structure of the films.

3. RESULTS & DISCUSSION

3.1 The different La molar concentrations

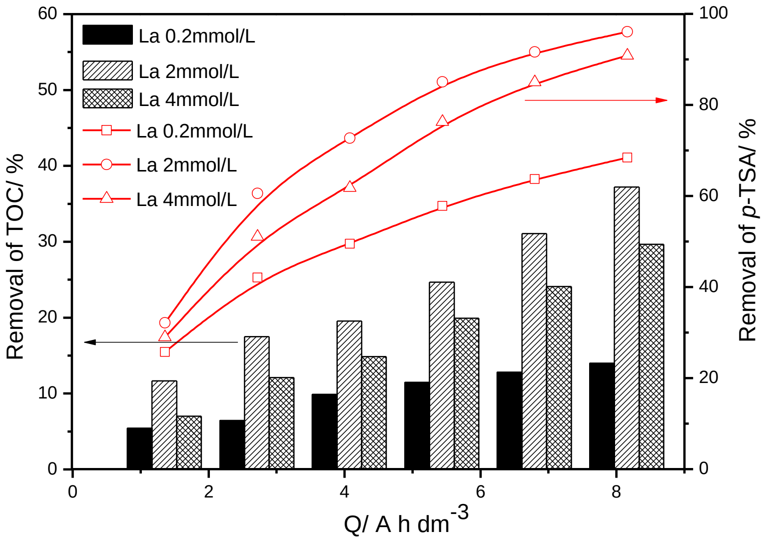

Figure 2. Removal rates of *p*-TSA and TOC by different molar concentration of La doped Ti/SnO_2-Sb_2O_3 electrodes

The maximum rate of *p*-TSA removal of La-doped Ti/SnO_2-Sb_2O_3 electrodes was achieved using a La doped molar concentration of 2mmol/L (Fig. 2). As shown in Fig. 3, rates of *p*-TSA removal were well fitted with first-order rate constants. The doped molar concentration of 2mmol/L La-doped electrode was 70.81% higher than using an electrode with 0.2mmol/L La (Table. 1). The same general trend in the rate of removal of TOC and *p*-TSA in solution with the different La moral concentrations of the electrodes was initially observed (Fig. 2). It also could be concluded that electrodes modified by La could not always exhibit a perfect performance on degradation. Although proper doped molar concentration of La (2mmol/L) could significantly improve the degradation efficiency of electrode, inappropriate doped concentration could lead a decrease in performance. Without suitable doped concentration of rare earth, adverse changes on the surface of modified electrode would result in the decrease of specific surface area and the reduction of concentration of oxygen free radicals (such as ·OH). As a result, for the perfect performance of the electrode with 2mmol/L La doped, other electrodes were not examined further in subsequent tests.

Table 1. Degradation kinetics constant (κ) of *p*-TSA removal by different molar concentration of La doped Ti/SnO_2-Sb_2O_3 electrodes

La molar concentration ($mmol·L^{-1}$)	κ ($L·mg^{-1}·min^{-1}$)	R^2
0.2	0.00141	0.94215
2	0.00483	0.98530
4	0.00282	0.99386

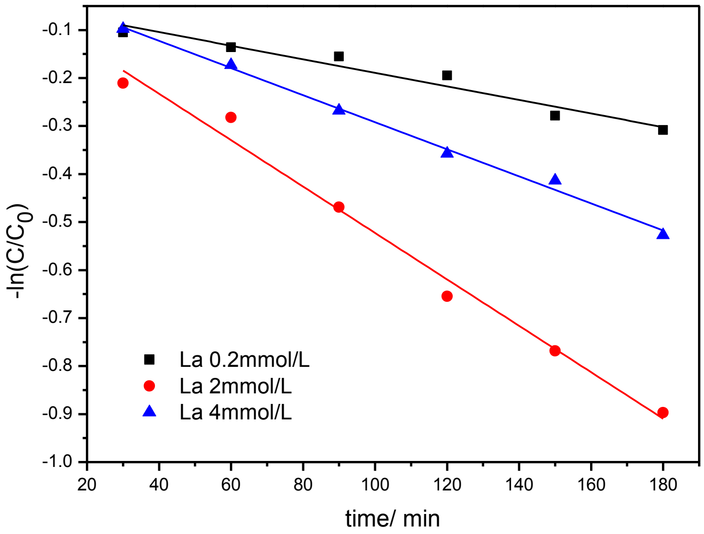

Figure 3. Pseudo-first-order kinetics fit of *p*-TSA removal by different molar concentration of La doped Ti/SnO_2-Sb_2O_3 electrodes

3.2 Degradation of p-TSA by different electrodes

A solution of 500 $mg·L^{-1}$ of *p*-TSA of pH 2.0 was electrolyzed at 30 $mA·cm^{-2}$ and with a room temperature to test its degradation efficiency by anodic oxidation with Ti/SnO_2-Sb_2O_3/PTFE-β-PbO_2 and Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2. Fig. 4 and 5 showed the removal rate of *p*-TSA, TOC, COD. Doped with La could slightly improve the removal rates of *p*-TSA and TOC. As one of important indexes, removal rate of COD exhibited the ability of electrode to mineralize. The Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 anode has the higher COD removal of *p*-TSA (59.40%), compared with Ti/SnO_2-Sb_2O_3/PTFE-β-PbO_2 electrode, whose COD removal is 46.50%. as shown in Fig. 5. Therefore, Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 electrode possessed excellent mineralization to target contaminant (*p*-TSA), compared with undoped anode (Ti/SnO_2-Sb_2O_3/PTFE-β-PbO_2 electrode). Combined the analysis of two figures above (Fig. 4 and 5), some conclusions could be inferred that La-doped could accelerate the degradation ratio of electrocatalysis intermediates and then enhance the mineralization efficiency.

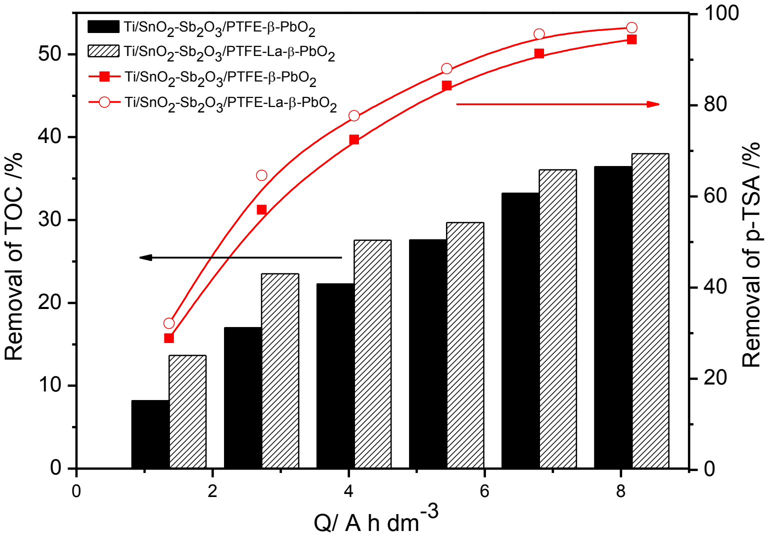

Figure 4. Removal rates of *p*-TSA and TOC by Ti/SnO_2-Sb_2O_3/PTFE-β-PbO_2 and Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 electrodes

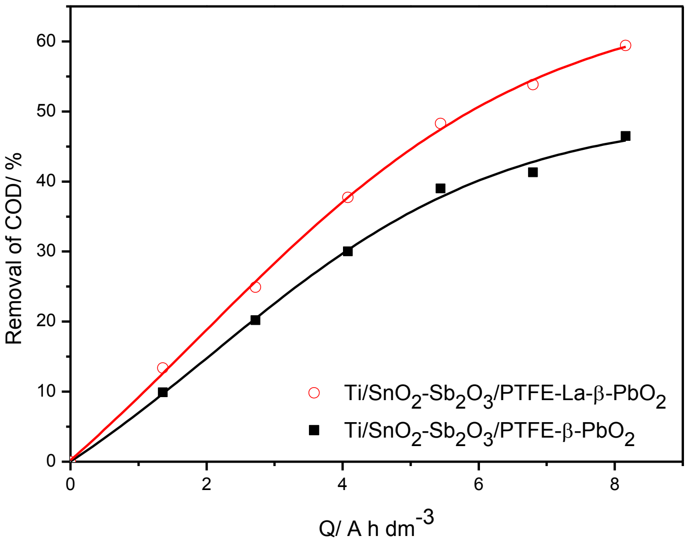

Figure 5. Removal rates of COD during the electrolysis by Ti/SnO_2-Sb_2O_3/PTFE-β-PbO_2 and Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 electrodes

3.3 Characterization of electrodes and analysis of doped mechanism

XRD and SEM were employed for characterize Ti/SnO_2-Sb_2O_3/PTFE-β-PbO_2 and Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 electrodes. The XRD spectrums and SEM images were shown in Fig. 6 and Fig. 7, respectively. As can be seen in Fig. 6, compared with the PbO_2 film of Ti/SnO_2-Sb_2O_3/PTFE-PbO_2, there had no new mineral phases on the PbO_2 film with the addition of La. This phenomenon can be explained by the low amount of La or the solid solution composed by La_2O_3 and PbO_2 for the doping of La into the crystal lattice of PbO_2 as a kind of replacement or interstitial material [21, 22].

Furthermore, the addition of La partially broadened the diffraction intensity of β-PbO_2 on the film of electrodes. That was because the introduction of La^{3+} (0.103nm), which had bigger ionic radius than Pb^{4+} (0.0775nm), expanded the crystal cell in the progress of doped [23]. What's more, the morphology of Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 electrodes, as shown in Fig. 7, was compact, uniform, and presented a typical mushroom shaped. The comparison between the SEM image of Ti/Sb-SnO_2/PTFE-β-PbO_2 and that of Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 electrode supported the speculation from XRD visually. Little holes in the surface of Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 electrode could help improve the specific surface area of electrodes, exposed more active sites and promote the reaction mass transportation. The porous film of Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 contributed to the ability of electrocatalysis.

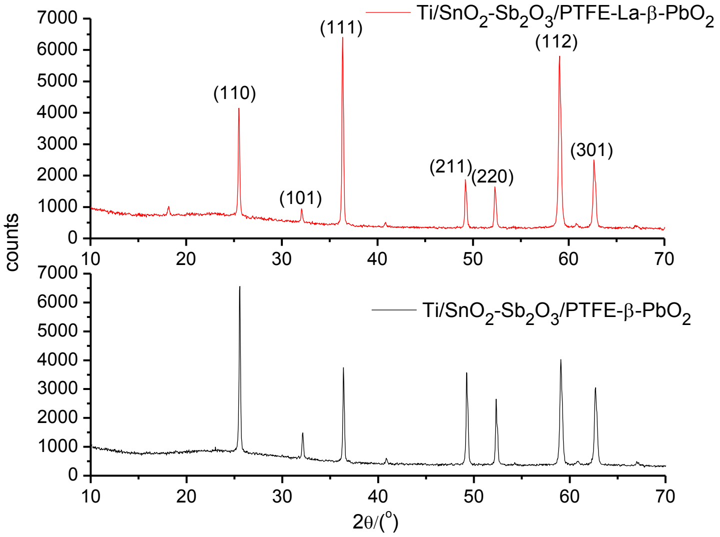

Figure 6. XRD spectrums of Ti/SnO_2-Sb_2O_3/PTFE-β-PbO_2 and Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 electrodes

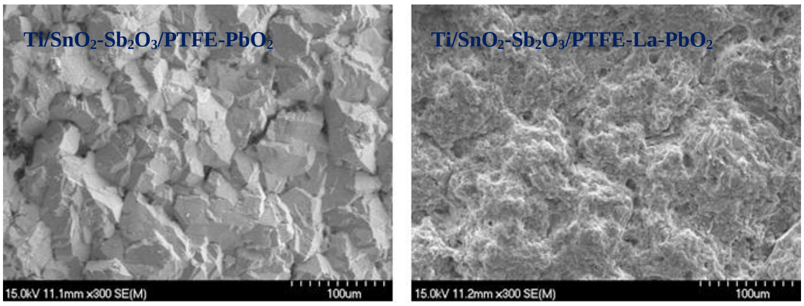

Figure 7. SEM images of Ti/SnO_2-Sb_2O_3/PTFE-β-PbO_2 and Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 electrodes

4. CONCLUSION

Typical rare earth doped lead dioxide electrode (Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2) was prepared by the thermal decomposition electrodeposition technique. It was can be proved that the inference of co-doped with PTFE-La_2O_3 on the electrocatalytic properties of Ti/SnO_2-Sb_2O_3/PTFE-PbO_2 was positive. La as a dopant brought remarkable promotion to the mineralization efficiency of intermediates of *p*-TSA stimulated wastewater (With La bearing, the removal rates of COD and *p*-TSA during 3 h electrolysis at the current density of $30mA\cdot cm^{-2}$ were 59.40% and 95.00%, respectively, with the instantaneous current efficiency being 49.22%-18.13%). What's more, the rates of *p*-TSA removal were well fitted with first-order rate constants. According to SEM images and XRD spectrums, PTFE-La_2O_3 co-doped had advanced function on the promotion of electrocatalysis and the modification of Ti/SnO_2-Sb_2O_3/PTFE-β-PbO_2 film structure. The porous film of Ti/SnO_2-Sb_2O_3/PTFE-La-β-PbO_2 improved the specific surface area, exposed more active sites, promoted mass transportation and enhanced the efficiency of electrocatalysis.

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