Preparation and Characterization of Titanium Based PbO₂ Electrodes Doped with Some Common Elements

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Abstract: Four kinds of PbO₂ electrodes were prepared by electrochemical deposition and three of them were doped by Fe, Ni, and Ag, respectively. The characters of the electrodes were analyzed by SEM, XRD, accelerated life tests, and linear scanning voltammetry. The results show that the electrode surfaces are covered by quadrangular β-PbO₂ crystals. The average grain sizes of the undoped PbO₂ electrode and Ni-doped PbO₂ electrode are similar and smaller than that of the Fe-doped PbO₂ and Ag-doped PbO₂ electrodes. The Fe-doped PbO₂ electrode has the longest accelerated test life due to its dense surface. The LSV tests show that the Ni-doped PbO₂ electrode possesses the highest oxygen evolution potential. From the phenol electrolysis, the Ni-doped PbO₂ electrode demonstrated the best performance in COD removal efficiency, average current efficiency, and energy consumption.

Key words: PbO₂ electrode; doping; accelerated life; oxygen evolution potential; phenol wastewater degradation

In recent years, the electrochemical oxidation treatment has gained more and more attention for its potential application in the degradation of refractory pollutants[1-9]. In the electrochemical oxidation method, one of the most crucial components is the anode where the decomposition reactions of pollutants take place. Currently, the most typical electrodes are dimensionally stable anodes (DSA) and boron doped diamond (BDD) [4,10-12]. The DSA electrode is used widely due to the easy preparation and cost-efficiency, e.g. PbO₂, SnO₂ [13-16], IrO₂ [17] and RuO₂ [18].

Among these DSA electrodes, PbO₂ is considered as an excellent metal oxide electrode because of its lower price compared to noble metals, chemical stability in corrosive media, and relatively high over-potential for the oxygen evolution reaction. Many attempts have been made on the enhancement of PbO₂ in order to further improve the performance of the PbO₂ electrode in the application. A frequently used method is to dope the PbO₂ layer with some materials [19]. For instance, Amadelli et al. [20] prepared the F-PbO₂ electrodes and found that the oxygen evolution process of the F-PbO₂ electrodes shifted to higher potentials and the current efficiency of the formation of O₂ rose at a given current density, compared to unmodified PbO₂. Song et al. [21] used cerium nitrate as the dopant and obtained the PbO₂-CeO₂ electrode, which has excellent performance in the accelerated life test and the antibiotic wastewater treatment. Zhou et al. [22] used the fluorine resin as the dopant to prepare the PbO₂ electrode and similar results like Song’s work were obtained.

Phenols are aromatic compounds with one or more hydroxyl groups attached to the aromatic ring and are found as wastes from a variety of industries. The oxidation removal of phenol has been of particular interest because of their high yield in industrial effluents [23]; therefore, phenol was chosen as the probe in the electrochemical oxidation process.

In this work, three familiar elements, including Ni, Fe, and Ag were applied as dopants to prepare PbO₂ electrodes with Ti/Sb-SnO₂ by electrochemical deposition. X-ray fluorescence (XRF), scanning electron microscopy (SEM)
and X-ray diffraction (XRD) were used to examine the changes of the coating of these electrodes. The electrochemical analysis (including linear scanning voltammetry, accelerated life test, and electrochemical degradation) of the electrochemical performance was used to determine whether these changes result in improvement of the doped PbO₂ electrodes.

1 Experiment

1.1 Electrode preparation

Titanium plate (99.6% purity) with thickness of 1.0 mm was used in this study (BaoTi Co. Ltd, China). All the chemicals used were the analytical reagent. The deionized water used was produced by water purifier (EPET-40TF, EPET Co. Ltd, Nanjing, China).

Prior to the preparation process, Ti plates with a dimension of 5 cm×8 cm were mechanically polished by 1000-grid sand papers, and rinsed by deionized water. Then, the foils were immersed into a mixture of acetone and 1 mol·L⁻¹ NaOH (1:1 v/v) in an ultrasonic cleaner (KQ2200DB, 80 W, 40 kHz, Kunshan Ultra Co. Ltd, Jiangsu, China) to remove organic compounds from the surface, etched in 10 wt% oxalic acid at 98 °C for 2 h, and then washed by deionized water.

The Ti/Sb-SnO₂/PbO₂ electrode was prepared by dip-coating plus thermal deposition for the inner coating layer (Sb-SnO₂) and electrochemical deposition for the outer layer (PbO₂). The precursor solution for the inter metal oxide layer was prepared by dissolving 10% SnCl₄·6H₂O and 1% SbCl₃ in a solution consisting of 10 mL n-butanol, 10 mL iso-propanol, 10 mL ethanol and 2 mL hydrochloric acid (37%). The precursor solution must be freshly prepared and used due to its poor stability. The titanium plate was brushed by the precursor solution, and then rinsed by deionized water.

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1.2 Electrode characterization

The electrochemical degradation was performed in a two electrode cell. The stainless steel plate with a dimension of 5 cm×8 cm was used as the cathode, and the as-prepared electrodes were used as the anodes. The distance between the two electrodes was 2.0 cm. The solution’s temperature was controlled by the circular water bath and thermostat. The power was supplied by a WYK-303B electrical source.

In the treatment process, after 450 mL phenol wastewater (1000 mg·L⁻¹ phenol and 1 mol·L⁻¹ Na₂SO₄ as the supporting electrolyte) was added into the stainless steel reactor, the stirring and controller systems were turned on. The process was carried out under a constant current condition and the duration of electrolysis was 2 h. For the UV-vis and COD analyses, the wastewater was sampled for every half hour during the treatment.

The COD removal efficiency was calculated by the following formula:

\[
\text{Removal efficiency} = \frac{A_0 - A_t}{A_0} \times 100\% \tag{1}
\]

where \( A_0 \) is the COD value of initial wastewater and \( A_t \) is the COD of the solution at the given time \( t \).

The average current efficiency (ACE) was calculated by the following equation:

\[
\text{ACE} = \frac{(\text{COD}_0 - \text{COD}_t)FV}{8It} \times 100\% \tag{2}
\]

where \( \text{COD}_0 \) and \( \text{COD}_t \) are the chemical oxygen demand at the initial and the reaction time \( t \) (gO₂·L⁻¹), respectively. \( I \) is the current (A), \( F \) is the Faraday constant (96,487 C·mol⁻¹), \( t \) is the treatment time (s), and \( V \) is the volume of the wastewater (L).

The energy consumption (EC), expressed in kWh·kg COD⁻¹, was calculated by the following equation:

\[
\text{EC} = \frac{UIt}{3.6(\text{COD}_0 \text{- COD}_t)V} \tag{3}
\]

where \( U \) is the voltage applied (V).
2 Results and Discussion

2.1 Surface morphology

Fig. 1 shows the SEM images of various Ti/SnO2-Sb/PbO2 electrodes. All the 4 different electrodes of Ti/SnO2-Sb/PbO2 have uneven deposits, which provide more surface areas and potentially increase the electrode efficiency, and thus the application potential in wastewater treatment is improved. The shape is quadrangular for the undoped PbO2 electrode, as shown in Fig. 1a. But there are some areas (black spots) which are not fully covered with the PbO2. The Ni-doped PbO2 electrode surface is denser than the undoped PbO2 electrode surface. The quadrangular grains of the former are clearer than the latter, and there are some cavities in the quadrangular grains as shown in Fig. 1b. The Fe-doped PbO2 electrode has the densest surface among the four electrodes and its average grain size is bigger than that of the undoped PbO2 and Ni-doped PbO2. The Ag-doped PbO2 electrode has a similar grain size compared with the Fe-doped PbO2. Its surface is less denser and had many cracks.

2.2 XRD analysis

The XRD patterns of the 4 Ti/SnO2-Sb/PbO2 electrodes are shown in Fig. 2. There are no diffraction peaks of the doping elements, because their dosages in the PbO2 film are too low to be detected by XRD. This is further confirmed by XRF analysis, in which no doping elements are identified.

Two types of crystallites can be distinguished on the surface: small fraction of α-PbO2 crystals and the dominant β-PbO2 crystals. The main crystal planes for the undoped PbO2 electrode are β (110) at 31.67º and β (301) at 62.20º, which is consistent with the results reported by Kong et al. For the Ni-doped PbO2 electrode, it has the similar spectra with the undoped PbO2 electrode. But the angle positions of the two crystal planes are slightly shifted to 31.77º and 62.27º, respectively. And the diffraction intensity of the Ni-doped PbO2 electrode in these two positions is higher than the undoped PbO2 electrode, indicating the former has a better degree of crystallinity of PbO2. The main crystal planes for the Fe-doped PbO2 electrode are β (110) at 25.34º and β (211) at 49.04º. The main crystal planes for the Ag-doped PbO2 electrode are β (301) at 62.40º and β (211) at 49.00º. The 4 electrodes have their main crystal planes which are different from each other. The reason for this phenomenon is the doping in the electrochemical deposition. Thus, the doping process affects the growth of PbO2 and changes its growth orientation, resulting in a change of its crystal plane.

The average crystal size of PbO2 particles can be calculated from the XRD data according to Scherrer formula. The average crystal size is 27.78, 29.75, 33.11 and 34.84 nm for undoped, Ni-, Fe-, and Ag-doped PbO2 electrodes, respectively. It can be concluded that the undoped PbO2 electrode has the largest true surface area, followed by the Ni-doped, Fe-doped and Ag-doped PbO2 electrode.

2.3 Accelerated test life

Fig. 3 shows the curves of the potential versus time for the 4 Ti/SnO2-Sb/PbO2 electrodes in which all the curves have a similar pattern. There is a first platform period around 2.5~3.1 V. In this period, the potential is relatively stable which can be contributed to the steady consumption process of the PbO2 layer. When the potential rises to 6~8 V, the second platform period is shown. In the second platform period, the potential can no longer be maintained within a small interval, and a significant potential variation was observed instead. This may be due to the inner layer consumption. If the coating on the titanium base is used up, it will result in a rapid increase of the potential, which indicates the inactivation of the electrode. As we set the 10 V (vs Ag/AgCl) as the failure criteria, the service life is 116, 100.5, 99.1 and 52 h for Fe-, undoped, Ni-, and Ag-doped PbO2 electrodes, respectively.
Fig. 3 Accelerated life tests of various PbO₂ electrodes in 3 mol·L⁻¹ H₂SO₄ solution under 1 A·cm⁻²: (a) undoped PbO₂, (b) Ni-doped PbO₂, (c) Fe-doped PbO₂, and (d) Ag-doped PbO₂.

It is noted that the Fe-doped PbO₂ electrode has the longest first platform period among the 4 tested electrodes. The Fe-doped PbO₂ electrode has a relatively lower electrode (surface) area due to its larger grain size, which reduces the electrolysis diffusion to the titanium base. In addition, the first platform period of the Ni-doped PbO₂ electrode is longer than that of the undoped PbO₂ electrode which means the former’s stability is better than the latter. This may be explained that the Ni-doped PbO₂ electrode has a denser surface than the undoped PbO₂ electrode, which can prevent the electrolysis diffusion and then reduces the PbO₂ layer consumption rate.

The actual life of the modified electrodes can be calculated from the relationship between the electrode service life (SL) and the current density [26],

\[ SL \sim \frac{1}{i^n} \] (4)

where \( n \) ranges form 1.4 to 2.0. Assuming an average \( n \) of 1.7 for the electrode, the service lives are predicted to be 8.91, 8.64, 14.1 and 4.58 for the undoped, the Ni-doped, the Fe-doped and the Ag-doped PbO₂ electrode, respectively, under the conditions of 20 mA·cm⁻² current density in the actual conditions.

2.4 Linear scanning voltammetry

Oxygen evolution potential is a critical parameter for the anode activity [27]. Fig. 4 shows the linear scanning voltammetry curve of the 4 PbO₂ electrodes in 1 mol·L⁻¹ H₂SO₄ solution at a scan rate of 50 mV·s⁻¹. It is found that the doped PbO₂ electrodes have higher oxygen evolution potentials than the undoped PbO₂ electrode. Among the doped PbO₂ electrodes, the Ni-doped PbO₂ electrode has the highest oxygen evolution potential of 2.10 V at 1.0 mA·cm⁻². Therefore, the Ni-doped PbO₂ electrode theoretically should have a better performance in the electrochemical degradation of organic contaminants in water and/or wastewater.

2.5 Phenol degradation

Fig. 5 shows the COD removal efficiency for the elec-

![Diagram](image)

Fig. 4 Linear scanning voltammetry curve of various PbO₂ electrodes in 1 mol·L⁻¹ H₂SO₄ solution at a scan rate of 50 mV·s⁻¹: (a) undoped PbO₂, (b) Ni-doped PbO₂, (c) Fe-doped PbO₂, and (d) Ag-doped PbO₂.

![Diagram](image)

Fig. 5 Phenol degradation by the 4 PbO₂ electrodes: (a) COD removal efficiency, (b) ACE, and (c) EC.

![Diagram](image)
has the best performance by removing 75% of COD from the solution in 2 h, then followed by the undoped, the Fe-doped and the Ag-doped PbO₂ electrodes. The best performance of Ni-doped PbO₂ electrode is likely resulted from the combination of its larger surface area and the highest oxygen evolution potential. It is interesting to note that the undoped PbO₂ electrode has a second-best performance in phenol degradation. This suggests that the oxygen evolution potential is not the only parameter responsible for the organic degradation, and the anode surface area, for example, is another critical factor to determine the overall performance of the electrolysis process. This presumption can be further verified by the poor performance of the undoped PbO₂ electrodes, where the lower surface areas are observed, as shown in Fig.1.

In addition, electrode properties like the average current efficiency (ACE) and the energy consumption (EC) are found useful in evaluating the electrodes' performance for the degradation of phenol. Fig.5b and 5c show the ACE curves and EC curves, respectively. The Ni-doped PbO₂ electrode has the highest oxygen evolution potential which is 2.10 V at 1.0 mA·cm⁻². The undoped PbO₂ electrode and Ni-, Fe-, and Ag-doped PbO₂ electrodes are similar and smaller than that of the Fe-doped and Ag-doped PbO₂ electrodes.

3 Conclusions

1) 4 Kinds of PbO₂ electrodes are prepared by thermal decomposition and electrochemical deposition including an undoped PbO₂ electrode and Ni-, Fe-, and Ag-doped PbO₂ electrodes.

2) The surfaces of the electrodes are mainly covered with quadrangular β-PbO₂ crystals and a small amount of α-PbO₂. The average grain sizes of the undoped PbO₂ and Ni-doped PbO₂ electrodes are similar and smaller than that of the Fe-doped and Ag-doped PbO₂ electrodes.

3) The service life is 116, 100.5, 99.1 and 52 h for Fe-, undoped, Ni-, and Ag-doped PbO₂ electrodes, respectively. The Fe-doped PbO₂ electrode has the longest service life due to its dense surface.

4) The LSV test shows that the oxygen evolution potentials of the doped electrodes are higher than that of the undoped electrode. The Ni-doped PbO₂ electrode has the highest oxygen evolution potential which is 2.10 V at 1.0 mA·cm⁻².

5) During the process of the phenol electrolysis, the Ni-doped PbO₂ electrode has the best performance by removing 75% of COD from the solution in 2 h, then followed by the undoped, the Fe-doped and the Ag-doped PbO₂ electrodes. The ACE and EC analyses results are comparable to the COD decay tendency with good correlations for all the 4 electrodes.

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