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Electro-catalytic degradation of phenol on several metal-oxide anodes

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ABSTRACT

Three kinds of Ti-based multilayer metal-oxide electrode, including Ti/$SnO_2 + Sb_2O_3$/PbO_2, Ti/$SnO_2 + Sb_2O_3$/MnO_x and Ti/$SnO_2 + Sb_2O_3$/$RuO_2 + PbO_2$ electrodes, were prepared by thermal decomposition, and $SnO_2 + Sb_2O_3$ coatings were produced with a polymeric precursor method (PPM). The conversion of phenol was carried out with these electrodes as anodes under galvanostatic control. Samples during the electrolyses were characterized with UV–vis spectra and chromatography, and chemical oxygen demand (COD) and instantaneous current efficiency (ICE) for phenol degradation were also determined. The results show that phenol can be oxidized and degraded for all of the three anodes, and the oxidation reactions of phenol follow first-order kinetics, but there are considerable differences in the effectiveness and performance of electro-catalytic degradation. Phenol can be degraded relatively fast on the Ti/$SnO_2 + Sb_2O_3$/PbO_2 anode and the degradation rate of phenol is slower with the Ti/$SnO_2 + Sb_2O_3$/MnO_x electrode, and the slowest with the Ti/$SnO_2 + Sb_2O_3$/$RuO_2 + PbO_2$ electrode, whose apparent rate constants are 2.49×10^{-2}, 1.42×10^{-2} and 9.76×10^{-3} min^{-1}, respectively. The rates of electro-catalytic degradation relate to oxygen evolution potential, and the higher the oxygen evolution potential, the better the performance of electro-catalytic degradation. The potential for oxygen evolution at the Ti/$SnO_2 + Sb_2O_3$/PbO_2 anode is highest, then Ti/$SnO_2 + Sb_2O_3$/MnO_x, following Ti/$SnO_2 + Sb_2O_3$/$RuO_2 + PbO_2$. The accelerated life tests at 60 °C and in 1.0 mol L^{-1} aqueous H_2SO_4 with an anodic current density of 4.0 A cm^{-2} show that the service life is prolonged when the $SnO_2 + Sb_2O_3$ interlayer coating are inserted between Ti substrate and active layers.

1. Introduction

Phenol is present in wastewater from the manufacture of petroleum refineries, phenolic resins, formaldehyde resins, caprolactam textile, and some pharmaceutical processes. Due to its toxicity and difficulty to degrade, the presence of phenol becomes a considerable problem to environment and human health [1]. Attempts have been made to degrade phenol using various technologies and processes, such as photochemical reactions [2–4], ultrasonic reactions [5,6], activated carbon adsorption [7–9]. Electro-catalytic degradation has attracted more attention due to simplicity in structure and ease in operation [10–13]. Biodegradation for organic compounds would be highly economical for wastewater treatment, but biodegradation of phenol is more difficult. Although organics can be effectively degraded to CO_2 by electrochemical methods, practically, the complete degradation of phenol to CO_2 by an electrochemical technique will not be economical due to high-energy consumption. In fact, when phenol is degraded to aliphatic products, the wastewater will become more biodegradable and much less toxic [14]. Partial oxidation of phenol, a ring opening reaction of phenol, results in organic acids of a biological nutrient requiring less energy consumption. Thus, the partial oxidation of organic pollutants by electro-catalytic degradation will provide us a valuable pre-treatment technique for subsequent cheap biological treatment.

In an electrochemical treatment technique, electrode materials directly affect the effectiveness and performance of the electro-catalytic degradation [15–18]. A dimensionally stable anode (DSA) has been used for many years in the chlorine-alkali industry, and the electrode is generally prepared with a substrate usually titanium on which a thin layer of metal-oxide mixtures, $RuO_2 + TiO_2$, is deposited. Modified DSA electrodes with other metal oxides, such as IrO_2, PbO_2, MnO_x, SnO_2, Co_3O_4, have also been investigated in order to modulate their properties and broaden their use [19].

In our research, conventional metal oxides, such as PbO_2, MnO_x and RuO_2, were used, but there were some marked differences:

(1) The electrodes used in the research were a kind of multilayer metal-oxide anodes containing the $SnO_2 + Sb_2O_3$ interlayer.

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(2) The traditional method of preparing metal-oxide coatings was with alcohols as precursor solvents, while the method of preparing the $SnO_2 + Sb_2O_3$ interlayer in the work was a polymeric precursor method (PPM), that is, with polymeric precursor as a precursor solvent.

For multilayer metal-oxide electrodes, $Ti/SnO_2 + Sb_2O_3/PbO_2$, $Ti/SnO_2 + Sb_2O_3/MnO_x$ and $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$, the $SnO_2 + Sb_2O_3$ coating was used as an interlayer, whose major purpose is to improve the service life of the anodes.

In our previous work [20–23], several metal-oxide electrodes ($Ti/SnO_2 + Sb_2O_3/PbO_2$, $Ti/SnO_2 + Sb_2O_3/MnO_x$ and $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$) were prepared by a thermal decomposition technique, and surface morphology, microstructure and electro-catalytic activity of coatings were investigated. The main purpose of this work is to study the effects of different anode materials on phenol degradation.

2. Experimental

2.1. Preparation of three kinds of anode

The detail of the preparation method of the anodes can be found in Refs. [20,22]. A 3 mm × 3 mm × 0.5 mm titanium plate was used as support or substrate. Prior to deposition process, the titanium plate was treated by sandblasting, followed by a chemical treatment in hot 5% (w/w) NaOH solution for 1.0 h. Then, the plate was treated in hot 10% (w/w) oxalic acid for 1.0 h. Finally, the support was washed with purified water and dried at 120 °C.

The precursor solution for depositing the $SnO_2 + Sb_2O_3$ coating on the support was a polymeric precursor solution, prepared by dissolving citric acid (CA) in ethylene glycol (EG) at 60 °C, raising the solution temperature to 90 °C and dissolving $SnCl_4{\cdot}5H_2O$ and $SbCl_3$. The molar ratio of CA/EG/Me was 1/4.5/0.33, where Me refers to both tin and antimony ions and Sn/Sb molar ratio was 9/1. The precursor solution was quantitatively spread on the pretreated support and the coating was initially treated at 130 °C for 10 min. After that, it was annealed at 500 °C for 10 min. This procedure was repeated 10 times, and finally the support and coating was annealed for 60 min.

The precursor solution for preparing the PbO_2 active coating was a saturated aqueous solution of $Pb(NO_3)_2$ containing 2% (v/v) *n*-buanol. The solution was quantitatively spread on the $Ti/SnO_2 + Sb_2O_3$ sample, and the coating was initially treated at 80 °C for 10 min. Then, it was annealed at 480 °C for 10 min to obtain the oxides. The procedure was repeated 10 times, and at last the coating was annealed for 60 min.

The MnO_x or $RuO_2 + PbO_2$ coating was also prepared using a thermal decomposition method. The 50% (w/w) $Mn(NO_3)_2$ solution or $RuCl_3$ and $Pb(NO_3)_2$ (molar ratio 7/3) solution was deposited on the $Ti/SnO_2 + Sb_2O_3$ sample. The procedure was the same as previously described, except for the calcination temperature used was 400 and 500 °C, respectively.

2.2. Electro-catalytic degradation of phenol

The metal-oxide electrode described above was used as an anode and a copper plate as a cathode, and the distance between the

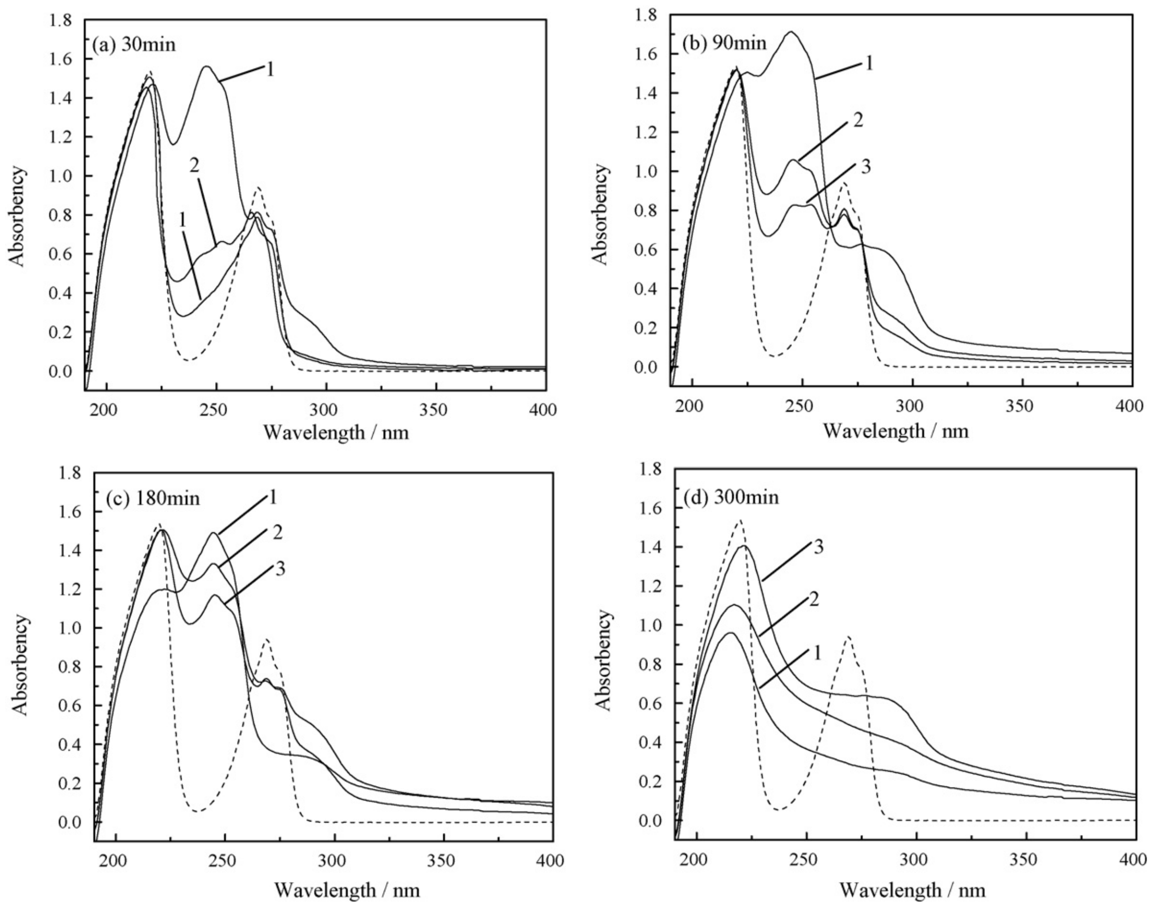

Fig. 1. UV spectra of the electrolyte at some electrolysis time for different electrodes. Dash line corresponds to the initial phenol solution. Full lines correspond to different anodes. (1) $Ti/SnO_2 + Sb_2O_3/PbO_2$, (2) $Ti/SnO_2 + Sb_2O_3/MnO_x$ and (3) $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$.

anode and cathode was set at 1.0 cm. Eighty millilitres of synthetic wastewater containing 200 mg L^{-1} phenol and 10 g L^{-1} Na_2SO_4 was charged in an electrolysis cell and the Na_2SO_4 solution was acted as a supporting electrolyte. The cell, immersed in a flowing water bath to keep it at 25 °C constantly, was set on a magnetic stirrer for continuous mixing. The operating current density was 15 mA cm^{-2}.

2.3. Determination of the current efficiency

The chemical oxygen demand (COD) method [24] was used for the determination of the current efficiency for the anodic oxidation of phenol. In this method, the COD was measured during electrolysis using a 5B-3 model accelerated COD analyzer and the instantaneous current efficiency (ICE) was calculated by the following equation:

$$\mathrm{ICE} = \frac{FV}{8I} \times \frac{\mathrm{d[COD]}}{\mathrm{d}t} \qquad (1)$$

where d[COD]/dt is the rate of COD change and COD values is expressed in g O_2 L^{-1}; t is the time of electrolysis (s), and I is the current (A), F the Faraday constant (C mol^{-1}) and V is the volume of the electrolyte (L).

2.4. Electrochemical measurements

The electrochemical characterization was conducted using a CHI-660B model electrochemical station (Shanghai Chenhua Instrument Ltd. Co.). The voltammetric curves were measured at 25 °C using the three-electrode cell: each of the three kinds of anodes as the working electrode at a time, an SSE (saturated $Hg/Hg_2SO_4/K_2SO_4$) as the reference electrode, and a platinum foil as the auxiliary electrode.

2.5. Accelerated lifetime test

The accelerated lifetime test was carried out in a double-compartment cell under galvanostatic conditions at 4.0 A cm^{-2} using a copper plate as a cathode; 1.0 mol L^{-1} H_2SO_4 was used as the electrolyte and the working temperature was 60 °C. The electrolysis time when the added value of the cell potential reached 5 V was regarded as the service life of the anode.

2.6. Analysis

The UV absorbency spectrogram at the wavelength range 190–400 nm was recorded using a TU1800-SPC UV-vis spectrometer.

The concentration of phenol was monitored by liquid chromatography which was carried out on a LCQ Deca XP MAX. Twenty microlitres of sample was injected, the separation was performed using an ODS-18 reversed phase column with methanol–water (30/70, v/v) as the effluent at a flow rate of 1 ml min^{-1} and a column temperature of 25 °C. An UV detector was used with the wavelength setting at 270 nm.

3. Results and discussion

3.1. Influence of anode composition on degradation rate of phenol and rate of COD removal

The influence of the anode composition ($Ti/SnO_2 + Sb_2O_3/PbO_2$, $Ti/SnO_2 + Sb_2O_3/MnO_x$ and $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$) on the degradation process of phenol was studied. Fig. 1 is UV absorbency spectrograms in the wavelength range 190–400 nm at some electrolysis time for different electrodes. The peaks of phenol at 270 nm decrease with prolonging electrolysis time, and the peaks of benzoquinone (BQ) at 245 nm grow in the initial period, then come down.

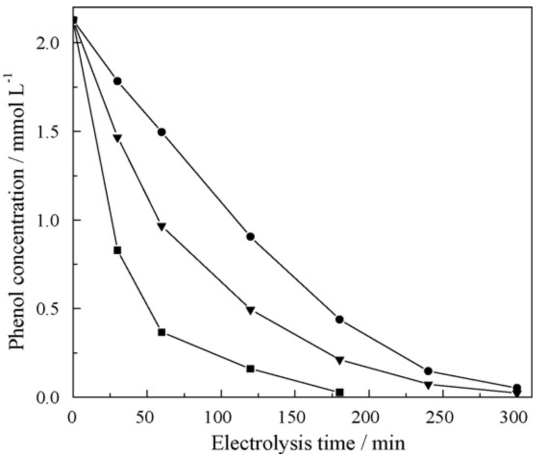

Fig. 2. Electrolysis time dependence of phenol concentration for the three anodes: (■) $Ti/SnO_2 + Sb_2O_3/PbO_2$, (▼) $Ti/SnO_2 + Sb_2O_3/MnO_x$, and (●) $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$.

The concentration of phenol was measured using HPLC and the variations of phenol concentration with electrolysis time for the three anodes are shown in Fig. 2. At same electrolysis time, the rate of electro-catalytic degradation of phenol is different for three kinds of anode. The reaction rate is fastest on the $Ti/SnO_2 + Sb_2O_3/PbO_2$ anode, while the reaction rate is relatively slow on the $Ti/SnO_2 + Sb_2O_3/MnO_x$ anode, and the slowest on the $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$ anode. Table 1 indicates that different electrodes exhibit different performance in the rate of electro-catalytic degradation of phenol.

For waste water treatment, the study on the variation of phenol concentration is not enough, because phenol can produce other intermediate compounds. In general, the degradation of phenol follows the sequences below [19,25,26]: (1) oxidation of phenol to other hydroxylated or oxygenated compounds, especially quinonic

Table 1
Apparent rate constants of phenol removal fitted by a first order model for different anodes

Anodes	k ($\times 10^2$ min^{-1})	R^2
$Ti/SnO_2 + Sb_2O_3/PbO_2$	2.49	0.9944
$Ti/SnO_2 + Sb_2O_3/MnO_2$	1.42	0.9886
$Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$	0.976	0.9872

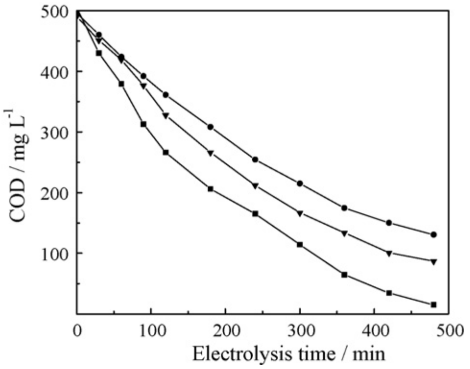

Fig. 3. Variations of COD with electrolysis time for the different anodes: (■) $Ti/SnO_2 + Sb_2O_3/PbO_2$, (▼) $Ti/SnO_2 + Sb_2O_3/MnO_x$, and (●)$Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$.

compounds (cyclic intermediates), (2) the ring opening reaction to form organic acids, and (3) mineralization of the organic acids to carbon dioxide. Therefore, the rate of COD removal should also be given attention.

The variations of COD with electrolysis time for the different anodes are shown in Fig. 3. For the $Ti/SnO_2 + Sb_2O_3/PbO_2$, electrode, not only the rates of degrading phenol are faster than the other electrodes, but also the rate of COD removal is also fast. When using the $Ti/SnO_2 + Sb_2O_3/PbO_2$ electrode as an anode, 59.3% COD removal can be achieved after the electrolysis time of 3.0 h in comparison to 45.7% and 37.9% COD removal obtained with $Ti/SnO_2 + Sb_2O_3/MnO_x$ and $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$ electrodes, respectively.

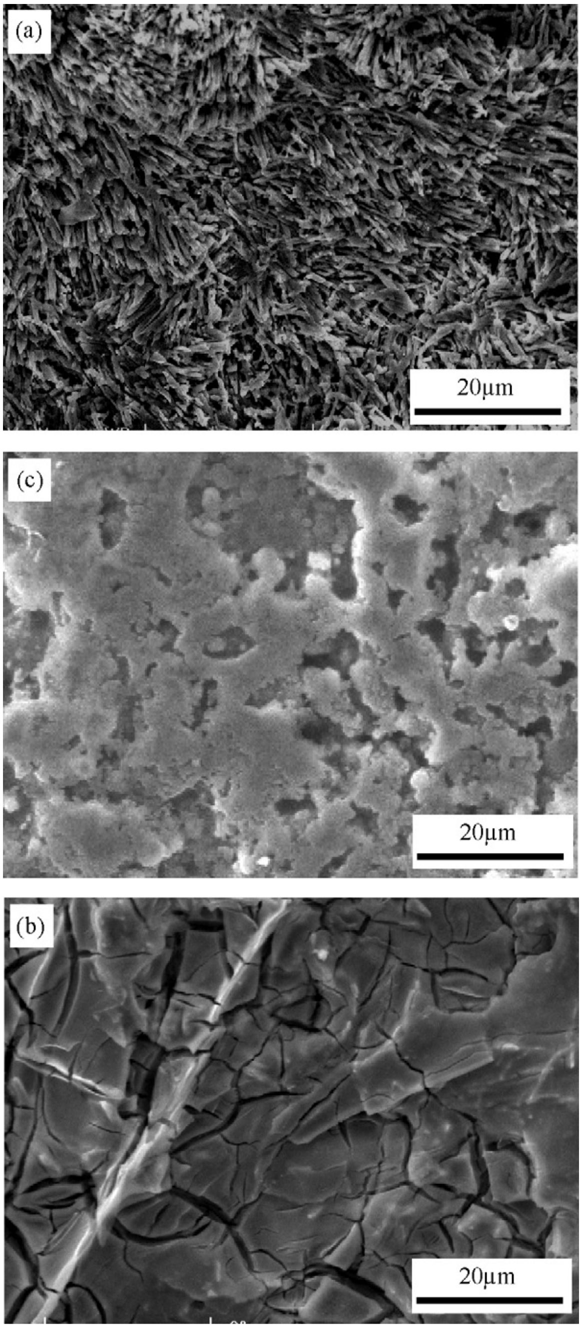

Fig. 4. SEM micrographics for different anodes: (a) $Ti/SnO_2 + Sb_2O_3/PbO_2$, (b) $Ti/SnO_2 + Sb_2O_3/MnO_2$ and (c) $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$.

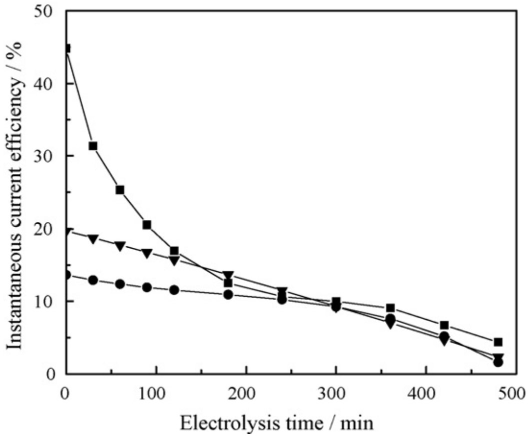

Fig. 5. Variations of instantaneous current efficiency with electrolysis time corresponding to the following anodes: (■) $Ti/SnO_2 + Sb_2O_3/PbO_2$, (▼) $Ti/SnO_2 + Sb_2O_3/MnO_x$, and (●) $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$.

In fact, the electrochemical oxidation of all organic compounds can be divided into conversion and combustion [27], and the mechanism for the electrochemical oxidation of organics depends on anode materials. At oxide anodes (MO_x) surface two states of "active oxygen" can be present which are (i) physisorbed "active oxygen", adsorbed hydroxyl radicals $MO_x(^{\bullet}OH)$, and (ii) chemisorbed "active oxygen", oxygen in the oxide lattice MO_{x+1}. The physisorbed "active oxygen" will cause predominantly the complete combustion of organics, Eq. (1), and chemisorbed "active oxygen", Eq. (2):

$$R + MO_x(^{\bullet}OH)_z \rightarrow CO_2 + zH^+ + ze + MO_x \tag{1}$$

$$R + MO_{x+1} \rightarrow RO + MO_x \tag{2}$$

The electrochemical characteristic of the $Ti/SnO_2 + Sb_2O_3/PbO_2$ electrode is relatively stable and physisorbed "active oxygen" is more. Therefore, the complete combustion of organics is predominant on the $Ti/SnO_2 + Sb_2O_3/PbO_2$ electrode and thus the degradation rate of phenol is relatively rapid. Chemisorbed "active oxygen" MO_{x+1} can be generated at other two anodes (MnO_x and $PbO_2 + RuO_2$) and will participate in the formation of selective oxidation products.

In addition to the composition of metal oxides, microstructure is an important factor for the performance of the metal-oxide anodes. The representative scanning electron microscopy micrographics for different electrodes presented in Fig. 4(a)–(c) show that the surface area is relatively large for the $Ti/SnO_2 + Sb_2O_3/PbO_2$ electrodes and relatively small for $Ti/SnO_2 + Sb_2O_3/MnO_2$ and $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$ electrodes. Larger surface area can

Table 2
Service life under an accelerated life-test condition for different anodes

Electrodes	Service life (h)
$Ti/SnO_2 + Sb_2O_3/PbO_2$	29.5
$Ti/SnO_2 + Sb_2O_3/MnO_x$	39.2
$Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$	8.4

The anodes without the $SnO_2 + Sb_2O_3$ interlayer deactivate rapidly.

Table 3
Service life for the $Ti/SnO_2 + Sb_2O_3/PbO_2$ anode preparing the $SnO_2 + Sb_2O_3$ coating with different precursor solvents

Precursor solvents	Service life (h)
Polymeric precursor	29.5
Ethanol	13.5
n-Butanol	6.5

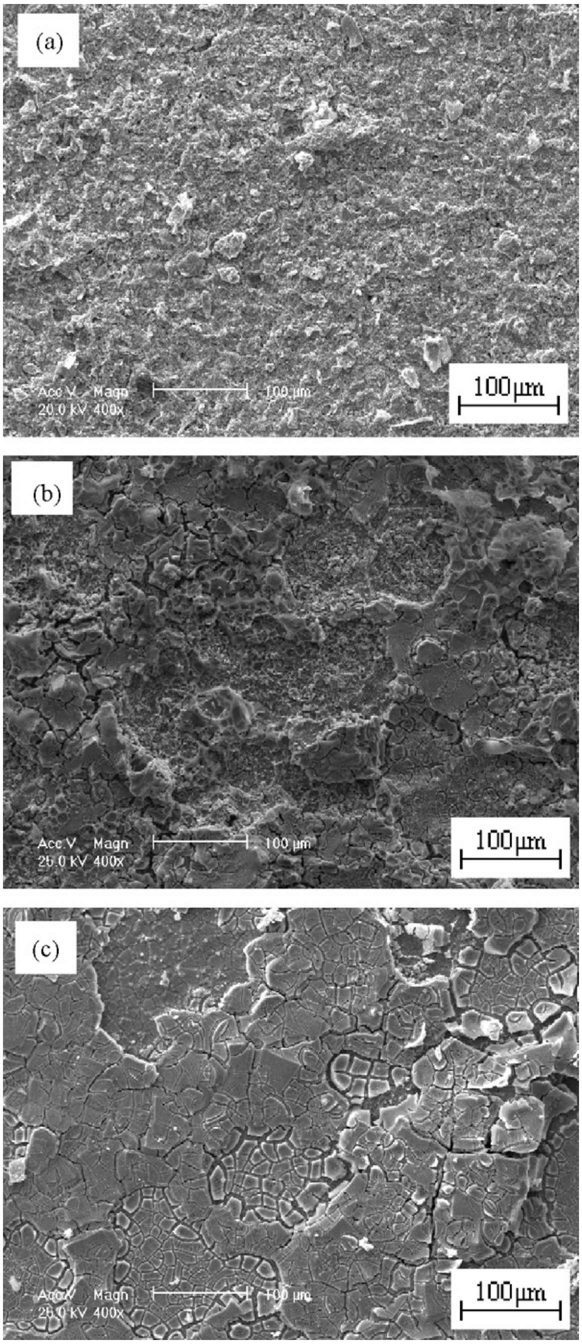

Fig. 6. SEM micrographics of $SnO_2 + Sb_2O_3$ coatings prepared with different precursor solvents: (a) polymeric precursor, (b) ethanol and (c) *n*-butanol.

contributes to the absorption of organics, so the rates of degradation increase.

3.2. Current efficiency of the degradation of phenol and service life for different anodes

Fig. 5 shows a trend of instantaneous current efficiency during the electro-catalytic degradation for the three anodes. There is a considerable difference in the effectiveness of the degradation. When the $Ti/SnO_2 + Sb_2O_3/PbO_2$ electrode was used as an anode, the value of ICE was relatively high, about 45% in the initial of reaction, and then decreases dramatically with the increase of electrolysis time. Relatively low-current efficiency (below 20%) was observed for the $Ti/SnO_2 + Sb_2O_3/MnO_x$ and $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$ electrodes.

Besides the rate and current efficiency of electro-catalytic degradation, the service life is an important performance. Accelerated lifetime tests were conducted at 60 °C and 1.0 mol L^{-1} in aqueous H_2SO_4 with an anodic current of 4.0 A cm^{-2}. The experimental results are shown in Table 2 and Table 3. It can be found that the service life of the multilayer metal-oxide electrodes containing the $SnO_2 + Sb_2O_3$ interlayer is longer than the anode without the $SnO_2 + Sb_2O_3$ coating. For the $SnO_2 + Sb_2O_3$ coating, the service life of the anode of preparing the $SnO_2 + Sb_2O_3$ coating with polymeric precursor method is longer than with alcohols as precursor. When preparing the interlayer with polymeric precursor method, the service life is in connection with active layers, and the service life of the $Ti/SnO_2 + Sb_2O_3/PbO_2$ anode is longest and the shortest is the $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$ anode.

In general, the deactivation of an electrode is usually associated to the modifications. For the multilayer metal-oxide anodes, the interlayer (the $SnO_2 + Sb_2O_3$ coating) plays an important role in connecting the Ti substrate and active layers and hampering penetration of the electrolyte towards the titanium substrate. The polymeric precursor method favors a morphological structure (Fig. 6a), which differs from the well-known mud-crack (Fig. 6b and c) obtained with alcohols as precursor, which offers a more agglomerated coating, leading to the construction of more robust electrodes compared with those prepared by alcohol precursors, so the layer might hamper penetration of the supporting electrolyte towards the titanium substrate and delays the formation of non-conductive TiO_2 layer. Therefore, the serve-life of the multilayer metal-oxide electrodes is prolonged.

3.3. Electrochemical characteristic of different anodes

Fig. 7 represents the polarization curves for oxygen evolution in 200 mg L^{-1} phenol solution at 25 °C for the

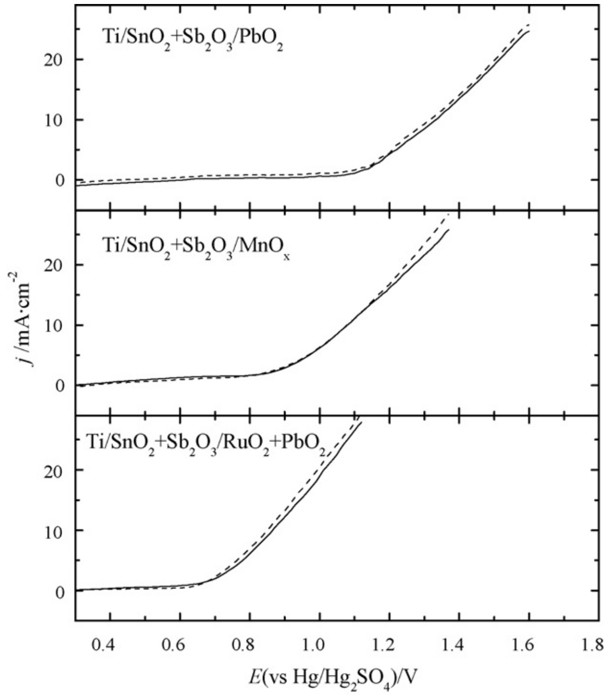

Fig. 7. Voltammogram of the anodes in the supporting electrolyte in the absence (dash line) and presence (full line) of 200 mg L^{-1} phenol at 25 °C; scan rate 1 mV s^{-1}.

three electrodes. According to the polarization curves, the threshold potential for oxygen evolution lies in the order: $Ti/SnO_2 + Sb_2O_3/PbO_2 > Ti/SnO_2 + Sb_2O_3/MnO_x > Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$.

In wastewater treatment, high-oxygen evolution voltage is especially desirable because anodic oxygen evolution in aqueous electrolyte represents an unwanted power loss and reduces the overall current efficiency. The $Ti/SnO_2 + Sb_2O_3/PbO_2$ anode with a high-oxygen evolution potential suggests that the radical reaction forming oxygen is probably restrained, and extend the lifetime of the hydroxyl radicals on the anode, which is favorable to the organic oxidation. In contrast, the lower oxygen evolution potential of the $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$ anode will shorten the lifetime of the hydroxyl radicals and hence hinder the oxygen transfer from the radicals for organic oxidation.

4. Conclusions

Phenol can be mineralized on the $Ti/SnO_2 + Sb_2O_3/PbO_2$, $Ti/SnO_2 + Sb_2O_3/MnO_x$ and $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$ anodes. The electrochemical characteristic and microstructure of anode materials affect remarkably the reaction rate and current efficiency of electro-catalytic degradation of phenol. The reaction rate is fastest on the $Ti/SnO_2 + Sb_2O_3/PbO_2$ anode, while the reaction rate is relatively slow on the $Ti/SnO_2 + Sb_2O_3/MnO_x$ anodes, and the slowest on the $Ti/SnO_2 + Sb_2O_3/RuO_2 + PbO_2$ anode. The instantaneous current efficiency also shows a same order.

Acknowledgments

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