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Degradation of Phenol in Aqueous Solution with Modified Ti/SnO_2-Sb Electrode

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Electrochemical degradation of phenol in aqueous solution was investigated over Ti/SnO_2-Sb anode prepared by coating dyrolysis method. The effect of Sb content on the structure and electrocatalytic performance of Ti/SnO_2-Sb anode had been studied. The surface coating structure was characterized by scanning electronic microscopy. The analysis showed that a limited amount of doping Sb (moral ratio of Sn:Sb = 100:5) could improve the surface structure of the layer and an over-doping of Sb had a negative impact. Furthermore, the effects of the applied current density and supporting electrolyte were studied by timing cyclic voltammetry and timing ultraviolet spectroscopy method. The experimental results indicated that about 100 % phenol was degraded at a constant current of 10 mA/cm^{-2} with the supporting electrolyte solution of sodium sulfate without a significant increase in potential within 12 h.

Keywords: Electrochemical degradation, Industrial wastewater, Phenol, Ti/SnO_2-Sb electrode.

INTRODUCTION

The oxidation of phenol compounds has been of particular interest because of their abundances in industrial effluent wastewater. However, aromatic chemicals are recalcitrant and toxic to biological treatment process. Alternatives have been reported for the destruction of toxic organic wastes, including Fenton oxidation[1,2], photochemical reactions[3,4], ozone oxidation, peroxide/ultraviolet spectroscopy-induced decomposition[5]. As an environmental friendly and promising method, electrochemical degradation is another alternative method for destroy aromatic organic, which has attracted wide attention in wastewater treatment[6-11]. Other advantages of electrochemical oxidation, including compatibility, simplicity in structure and operation, have raised concerns[12]. Specially, electrolysis can be used as a pretreatment technology in detoxifying ahead of bio-treatment[13].

In an electrochemical treatment technology, electrode materials are directly related with the effectiveness and performance of the electro-catalytic degradation usually. Traditional electrodes, such as graphite and nickel, show very poor current efficiency in organic degradation[14]. While the dimensionally stable anodes (DSAs), prepared by thermal deposition of a thin layer of metal oxides (RuO_2, IrO_2, SnO_2, PbO_2, *etc.*) on a base metal such as Ti, Zr, Ta, *etc*[15], show great performance. At present, so much work focused on the coating materials, such as PbO_2 and SnO_2, in terms of its high efficiency in detoxification and waste electro-degradation. However, the possible toxicity of Pb leaching from the working anode would hinder the actual application of PbO_2 electrode[16]. Recently, SnO_2 based electrode has attracted more attention, because it has several important technologically properties *e.g.*, good chemical stability and electrochemistry stability, good electrical conductivity and excellent chemical and corrosion resistance[17]. Recent studies indicated that co-doped SnO_2-based electrodes got better performance in an electrochemical process[18]. Tin oxide electrodes co-doped with antimony supported over titanium support have shown high reactivity towards dissolve organic pollutant[19].

In the present laboratory study, phenol was used as the model organic for electrochemical degradation. The aim of this work is to investigation of the structure and electrocatalytic performance of Sb doped Ti/SnO_2 electrode. The effect of Sb amount on the structure and electrocatalytic performance of Ti/SnO_2-Sb anodes had been studied. Meanwhile, the effects on the degradation, such as applied current density and supporting electrolyte, were optimized systematically with timing cyclic voltammetry (CV) and timing ultraviolet spectroscopy (UV) method. The modified electrode with SnO_2-Sb thin film was prepared by coating deposition technique. Meanwhile, scanning electron microscopy was used to characterize the morphology.

EXPERIMENTAL

All the chemicals and reagents used in experiments were of analytical grade and used without further purification. Distilled water was used throughout the work.

Electrode Preparation: In the present laboratory study, the titanium substrate was pretreated according to the following procedures before deposition. Firstly, Ti plate (1 cm × 1 cm × 0.2 cm) was polished using 40 and 320-grit sand papers, degreased in solution of 1:1 sodium hydroxide and *n*-acetone, etched in 15 % oxalic acid at 90 °C for 2 h, followed by a thorough washing with distilled water.

Coating SnO_2-Sb: The Ti/SnO_2-Sb electrode was prepared by the coating deposition in order to get a good adhesive metal oxide film. Dipped the pretreated Ti plate into the coating solution which consists of 2.106 g $SnCl_4·5H_2O(S)$, quantified $SbCl_3(S)$ (a variable molar ratios of Sn: Sb in the range of 100:0 to 100:25) with 0.2 mL 37 wt. % HCl in 3 mL *n*-propanol solution. The electrodes were then dried in an infrared lamp. Finally Ti plates were heated in a Muffle furnace (550 °C for 1 h) for coating pyrolysis to obtain the Ti/ SnO_2-Sb electrode.

Electrochemical removal of phenol: Using phenol as a model simulated wastewater. A three-electrode system was used in experiment with the modified Ti/SnO_2-Sb electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a pretreated Ti plates without coating film as the counter electrode. The gap between two electrodes was set to 10 mm. The electrolysis cell was 100 mL glass beaker. In the cell, the initial concentration of phenol solutions was 50 mg L^{-1}, with 0.25 mol L^{-1} supporting electrolyte of H_2SO_4, Na_2SO_4 and NaOH, respectively. The 50 mL solution was stirred with a magnetic stirring bar during electrolysis to promote the mass transfer. Samples were collected every one hour and prepared for analysis. All the experiments were carried out in duplicate.

Analysis procedures: An ultraviolet spectroscopy detector (ultraviolet spectroscopy-2550, Shimadzu Corp. Japan) was used with the wavelength setting at 270 nm to detection the concentration of phenol. Cyclic voltammetry of phenol was studying using an electrochemical workstation CH1760B (Shanghai Chenhua Instrument Co. Ltd. China) in a conventional three-electrode cell. Cyclic voltammetry measurement was performed at a scan rate 50 mV s^{-1} in 0.25 mol L^{-1} Na_2SO_4 solution at room temperature (25 °C). Furthermore, chronopotentiometry was also used to analysze the electrode stability and characters of the electrolysis during the experiments.

RESULTS AND DISCUSSION

Proposed function of Sb doping: Fig. 1 shows the morphology of the Ti/SnO_2-Sb electrode layers, obtained using the different Sb doping amount (0, 5, 15, and 25 %, respectively) under various magnifications. For all doping levels, the films have a cracked mud-like shape on surfaces compared to that of the control (0 %), which will enhance the effective surface area of the electrodes. The film prepared with 5 % Sb doped has a comparative flat structure and smaller interspaces. However, with the doping amount increasing, the surface of electrode becomes more and more rough and uneven. It was believed that the serious cracks would facilitate the formation of TiO_2 with poor conductivity and increase the resistance of the electrode surface during the service life tests[20].

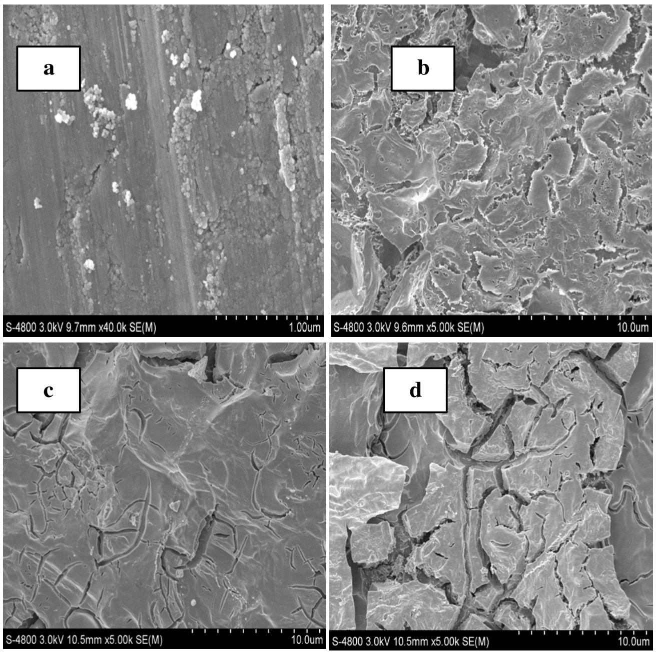

Fig. 1. Scanning electron micrographs of the electrodes; (SEM) (a) Ti/SnO_2 (b) 5 %Sb + Ti/SnO_2 (c) 15 % Sb + Ti/SnO_2 (d) 25 % Sb + Ti/SnO_2

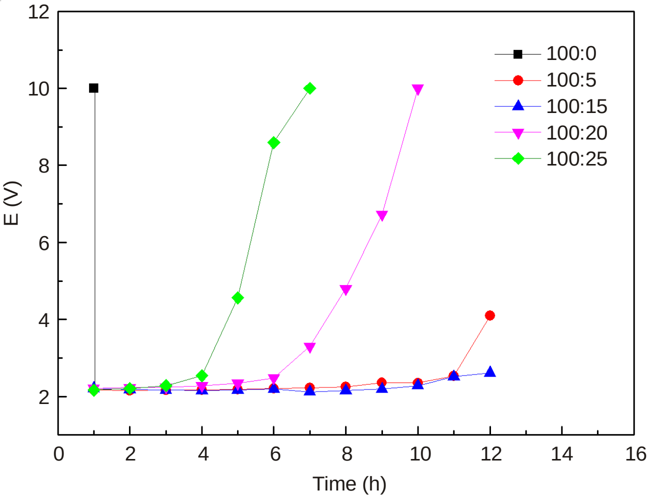

Fig. 2. Voltage changes in the process of phenol oxidation on the anode with different molar ratio of Sn:Sb

The anodes containing different amount of Sb performed considerable difference in the stability of the electrode (Fig. 2). The best result is obtained with the Sn: Sb ratio of 15 %, followed by the ratio of 5 % with the life time over 12 h. In the other ratio of Sb, the electrode turned to inactivity with a short time. However, the stability of the electrodes is much better than that of the control (0 %).

It had been reported that Sb^{3+} and Sb^{5+} replace Sn^{4+} in the rutile lattice and neither Sb_2O_3 nor Sb_2O_5 phase was detected in the XRD measurement[21]. The corresponding Sb^{3+} ions have a larger ionic radius (76 pm) than Sn^{4+} (69 pm) and could be responsible for the expansion of surface cracks. It may contribute to the introduction of Sb into the Ti/SnO_2 anode structure which change the SnO_2 crystal formation process and strengthen the adhesive force of the surface layer which lengthened the life-time of the electrode[22].

Fig. 3 displays the absorbance changes at 270 nm of the electrolyte oxidized on Ti/SnO_2-Sb anode with various molar ratio of Sn:Sb. The phenol removal rate of the Sb-doped electrode

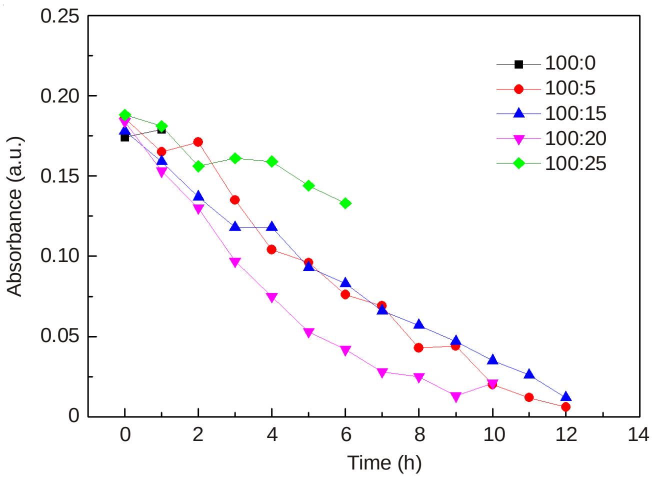

Fig. 3. Absorbance changes at 270 nm of the electrolyte oxidized on Ti/Sb-SnO_2 anode with different molar ratio of Sn: Sb

is much higher than that of the control (0 %). A maximum removal rate of phenol for Sb-doped Ti/SnO_2 electrodes is achieved using a Sn: Sb ratio of 5 %. Slower phenol removal rate is also produced with Sn: Sb ratio of 15 %. The result indicates that doping Sb can improve the catalytic activity of electrode. However, subsequent increase of the concentration of Sb does not favored to the degradation rate of phenol. It may attributes that the excess Sb doping amount destroys the integrity and order of the SnO_2 lattice. In view of electric performance, the Sn: Sb ratio of 5 % is chosen as the optimal condition in the following experiments due to the longer life-time and the higher degradation rates.

Effect of current density: Using 0.25 mol L^{-1} Na_2SO_4 as the supporting electrolyte the degradation curves of electrodes in 50 mL 50 mg L^{-1} phenol solution under various applied current density are shown in Fig. 4. From the experimental results, the efficiency of phenol degradation under 10 mA cm^{-2} is much higher than that of 5 mA cm^{-2} compared to the rapid inactive under 15 mA cm^{-2}. The removal efficiency of phenol increases with the current density increasing at the beginning. It is attributed to the improving rate of electron transfer, which speeds up the rate of direct oxidation of organic pollutant, while also accelerating the generation of hydroxyl radical rate. However, the higher current density may merely favor the anodic side reaction of oxygen evolution and decrease the efficiency. Fig. 5 shows that the highest life-time of 14 h is achieved at the 10 mA cm^{-2}, lower stability is obtained at the current density of 5 mA cm^{-2}, and the worst performance resulted from the 15 mA cm^{-2}, which is consistent with the Fig. 4.

The voltammetric behaviour of the Ti/SnO_2-Sb electrode at different current density is presented in Fig. 6. It can be observed that the voltammogram shapes are very close. The current density of the electrode gradually decreases while the oxidation potential increases gradually with the reaction proceeding. However, higher current density values are obtained with the 10 mA cm^{-2}. For the reaction of 1 h and scan cyclic voltammetry of 3 V, the corresponding electrode current density values are 100, 300 and 70 mA cm^{-2} when the operate current density values are 5, 10 and 15 mA cm^{-2}, which illustrates that higher activation properties achieve at 10 mA cm^{-2}.

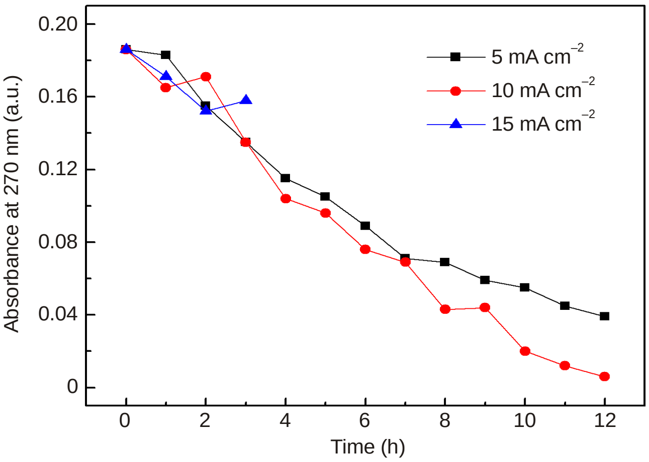

Fig. 4. Absorbance changes at 270 nm of the electrolyte in the process of electro-oxidation at different current density conditions

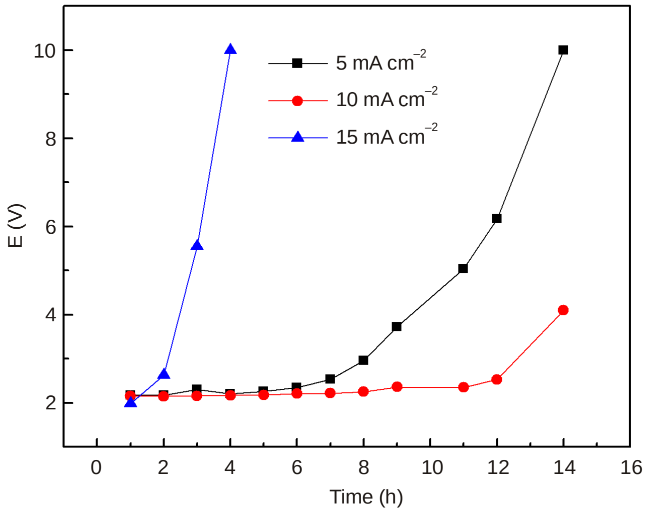

Fig. 5. Voltage changes in the process of phenol oxidation at different current density condition

In the vicinity of 0.9 V, an oxidation peak of phenol is observed in the amplification figure. At 5 mA cm^{-2}, the oxidation peak of the intermediate are appeared at 8, 9 and 10 h. There are oxidation peaks of the intermediate at the 11, 12 h under the operation of 10 mA cm^{-2} with the higher current density and lower potential values. This shows that the phenol removal is easier at 10 mA cm^{-2} than at 5 mA cm^{-2}.

Influence of the composition of electrolyte: In the following experiments, 0.25 mol L^{-1} H_2SO_4 (acidity), 0.25 mol L^{-1} Na_2SO_4 (neutral) and 0.25 mol L^{-1} NaOH (alkaline) were chosen as the electrolyte in a three-electrode system to study the phenol electro-catalytic degradation experiment. Cyclic voltammetry curves of the reaction and the amplification curve of part in the process are shown in Fig. 7. Fig. 7 (a_1), (b_1) and (c_1) show that the anodic current density decreases along with the reaction carried on. In acidic media, there is a fastest decrease on anode current density than that of others. The reduction speed of the anodic current density is stable along with the reaction process, indicating that degradation reactions are smoothly in neutral media. Meanwhile, the current density is relatively stable in alkaline media. The phenol oxidation peaks are obtained in the magnified cyclic voltammetry curves in acidic and neutral electrolytes, while that is not observed in

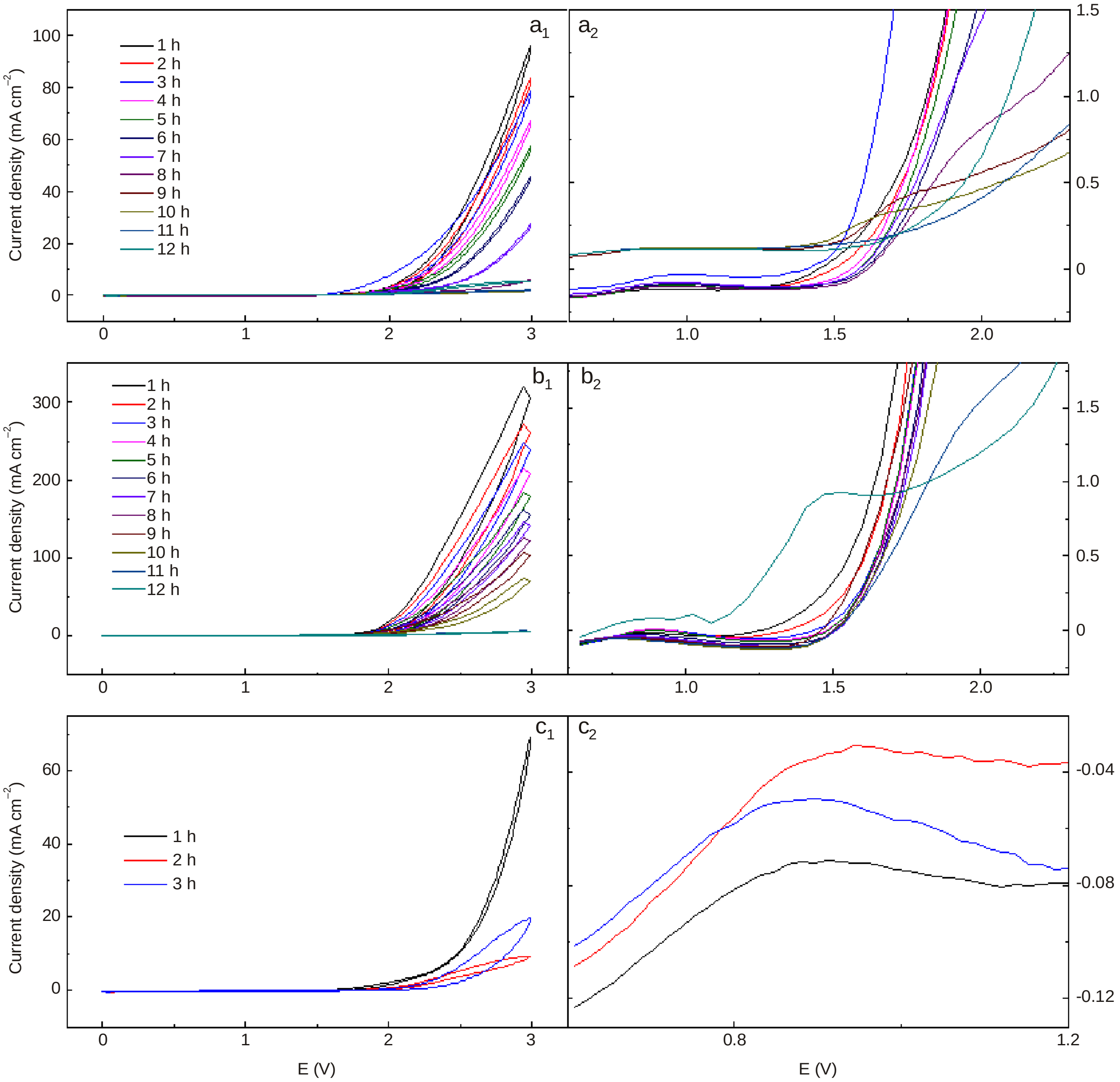

Fig. 6. Cyclic voltammetry curves and part amplifying curves at different current density conditions time: (a_1, a_2): 5 mA cm^{-2}; (b_1, b_2): 10 mA cm^{-2}; (c_1, c_2): 15 mA cm^{-2}

alkaline media throughout. The result shows that the phenol is oxidized indirectly instead of directly in alkaline condition. It is worth noting that phenol oxidation peak position is 0.9 V in the neutral media, and the peak in acidic media moves right to 1.15 V, which indicates that acidic media is not conducive to the degradation of phenol.

Fig. 8 showed the voltage changes in the process of phenol oxidation. The electrodes have been passivated and deactivated rapidly in the H_2SO_4 media. The reason is that the existence of the hydrogen ions in the solution may be suppressed the production of the reactive hydroxyl groups which results in insoluble polymeric adhering to the electrode surface. Therefore, the resistance increases rapidly and the electrode inactivates seriously.

Under neutral and alkaline conditions, the cell voltages have remained stable at 2 V until the reaction performed for 11 h. However, the electrodes with the Na_2SO_4 electrolyte have the trend of inactivation while the voltages remain stable in the NaOH electrolyte. The results suggested that the electrodes had higher activity in alkaline media due to the wealthy hydroxide converted to reactive hydroxyl which enhanced the oxidation of phenol. Meanwhile the removal rate of phenol is 100 % approximately with the neutral electrolyte, which is higher than 83.5 % in the alkaline electrolyte.

Conclusion

Thin films of antimony-doped SnO_2 on titanium substrate with a doping range of 0-25 mol % were prepared by coating

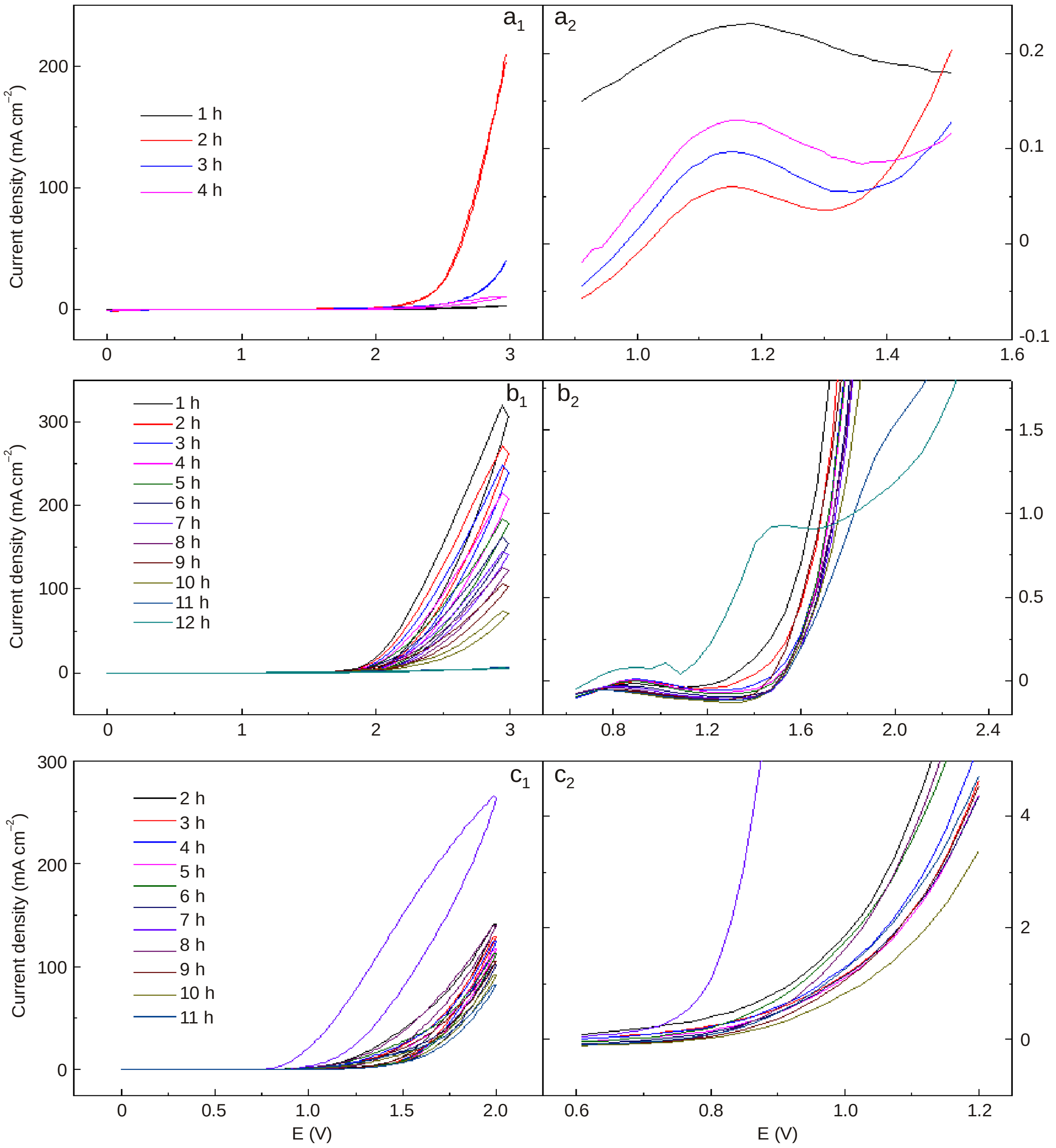

Fig. 7. Cyclic voltammetry curves and part amplifying curves in different electrolyte with time goes on: (a_1, a_2): H_2SO_4; (b_1, b_2): Na_2SO_4; (c_1, c_2): NaOH

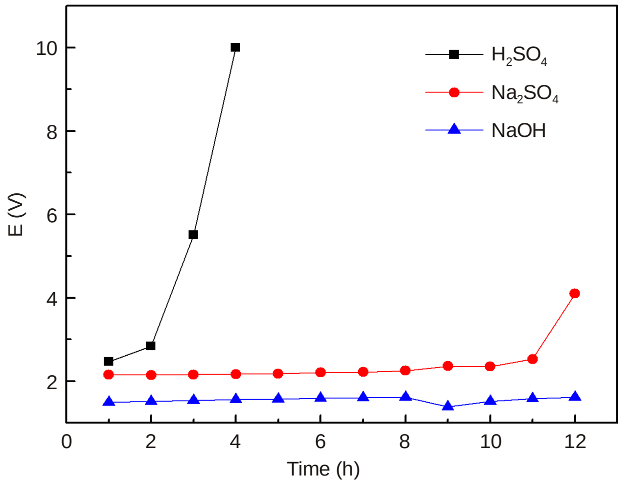

Fig. 8. Voltage changes in the process of phenol oxidation with different supportive electrolyte

dyrolysis method. The surface coating structure was characterized by scanning electronic microscopy (SEM). The analysis showed that a limited amount of doping Sb (moral ratio of Sn:Sb = 100:5) could improve the surface structure of the layer and an over-doping of Sb had a negative impact. Different performance for the phenol degradation at various current densities or the electrolyte was identified. It showed that the doping of the Sb into the Ti/SnO_2 anode changed the SnO_2 crystal formation process, enhanced the conductivity and resulted in good performance catalytic activity. The analytical results indicated that the most excellent stability anode was achieved with 5 % Sb amount at a constant current of 10 mA cm^{-2} with the supporting electrolyte solution of sodium sulfate. The higher degradation rate about 100 % of phenol was achieved by the modified electrode.

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