

## EPR study on Sb doped Ti-base SnO<sub>2</sub> electrodes

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Aquatic wastes, containing aromatics are recalcitrant and toxic toward conventional biological treatment. Electrochemical (EC) process is an alternative degradation method, which is attractive for low-volume application and environmental compatibility [1, 2]. Previous works have found that Sb doped Ti-base SnO<sub>2</sub> anode is quite interesting for its high oxygen evolution overpotential and attractive electro-catalytic characteristics [3, 4]. Some researchers also indicate that the electrochemical performance of SnO<sub>2</sub> electrode is strongly affected by doping species and doping amount of foreign atoms [5]. The investigation on relationship between SnO<sub>2</sub> electrode structure and its electro-catalytic performance is helpful for well understanding of EC process. While, few report about this has published till now. Crystal of SnO<sub>2</sub> in its pure form is a kind of *n*-type semiconductor and its electrical conductivity results from stoichiometric deviation (O:Sn ratio <2) [6], namely, oxygen vacancies, which might trap one electron and act as F<sup>+</sup> centre to be paramagnetic defects [7]. Electron paramagnetic resonance (EPR) spectroscopy is a powerful tool for the characterization of some paramagnetic defects in crystals and therefore it is employed at our present study to determine the crystal structure of coating compounds of several Ti-base SnO<sub>2</sub> anodes, the electrochemical degradation performance to target pollutant (phenol) was also investigated.

Four kinds of Ti-base SnO<sub>2</sub> electrodes with (1) Sb doped SnO<sub>2</sub> coating with Sn/Sb atom ratio of 100/6.5 (expressed as Ti/Sb(I)-SnO<sub>2</sub>), (2) Sb doped SnO<sub>2</sub> coating with Sn/Sb atom ratio of 100/10.7 (expressed as Ti/Sb(II)-SnO<sub>2</sub>), (3) a composite La-Sb-SnO<sub>2</sub> coating with Sn/Sb/La atom ratio of 100/6.5/4.8 (expressed as Ti/La-Sb(I)-SnO<sub>2</sub>), and (4) a composite Co-Sb-SnO<sub>2</sub> coating with Sn/Sb/Co atom ratio of 100/6.5/9.5 (expressed as Ti/Co-Sb(I)-SnO<sub>2</sub>) were prepared. The titanium plates which are selected as base metal for oxide-coated electrodes were firstly polished with 320-grit sand papers, then degreased in 40% NaOH solution at 80 for 2 h and finally etched in 6 N HCl solution at 90 for 1 h, followed by thorough washing with distilled water. The Ti/Sb-SnO<sub>2</sub> electrode was prepared by the following coating process: dip the pretreated Ti base plate into a coating solution consisted of SnCl<sub>4</sub>, SbCl<sub>3</sub> and HCl in *n*-butanol, then dry and heat it under air flow at an annealing temperature of 400 for 20 min. This process should be repeated more than 15 times and the final annealing temperature was 550 for 2 h. For the other-

search electrodes prepared, Chlorides of lanthanum or cobalt or manganese was added to the coating solution. These coatings were carried out in the same manner described above except the components of coating solution were different, and finally the quaternary metal oxide electrodes consisting of different elements were obtained. Under this preparation conditions, the coating structure of Sb<sup>5+</sup> doped SnO<sub>2</sub> crystals was obtained and it is confirmed by using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) [8].

Paramagnetic defects of the powder samples scraped from the electrodes surface were measured in the X-band region with a Bruker ER200D-SRC spectrometer. EPR parameters used were the following: *T* = 85 K, microwave frequency 9.51 GHz, modulated frequency 100 KHz, scan power 5.82 mW, modulated amplitude 0.05 mT, center field 0.342 T, scan width 0.05 T. Spin populations were calculated by comparing the integrated area of the signal with that of a standard strong pitch. Diphenyl picryl hydrazyl (DPPH) (*g* = 2.0036) was used as *g* marker for *g*-factor calculations.

In present experimental study, phenol with an initial concentration of 100 mg/L was selected as the organic substrate, and the volume of phenol solution in each EC cell was 100 ml. Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) at 0.25 M was used as supporting electrolyte. For each cell, a plate electrode of 6 cm<sup>2</sup> (2 × 3 cm) described above was used as the anode and stainless steel with the same area as the cathode with a distance of 1.5 cm between the two electrodes. A DC potentiostat with a voltage range of 0–30 V was employed as power supply for EC organic degradation. Electrolysis was performed under current control at 0.12 A. At the end of each run, after a pre-determined time of electrolysis, the solution in the cell was analyzed for phenol concentration.

Fig. 1 shows EPR spectra of the four samples. A peak-to-peak linewidth, *H*<sub>pp</sub>, of 0.39 mT and a *g* value of 2.0028 was obtained for all the samples. The same values of *g* mean the same electron paramagnetic resonance source since the nature of a paramagnetic centre is reflected primarily in its *g* value. So, our experiments imply that the EPR signals of the four samples could be caused by the same kind of defect existed in SnO<sub>2</sub> crystal lattice. In order to avoid the interferer of Ti<sup>3+</sup> which can also cause EPR signal, we prepared another powdered sample with SnCl<sub>4</sub>, SbCl<sub>3</sub> and HCl in *n*-butanol and tested its paramagnetic defects under the same experimental conditions. The same *g* value was obtained,

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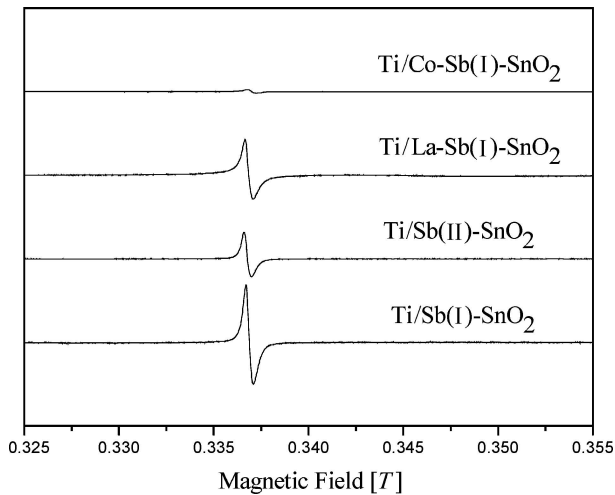


Figure 1 EPR spectrum of four electrodes samples.

indicates that the EPR signals aforementioned could not be brought by  $\text{Ti}^{3+}$ . Considering the fact that there are no unpaired electrons in the structure of either  $\text{Sn}^{4+}$  or  $\text{Sb}^{5+}$ , oxygen vacancy should be the only producer for EPR signals of all the samples. Also, the experimental results imply that foreign atoms incorporated into  $\text{SnO}_2$  crystal lattice may influence the concentration of paramagnetic centers since different EPR intensity was obtained for different doped  $\text{SnO}_2$  samples. Table I lists the EPR relative intensity of different samples, and the order can be expressed as  $\text{Ti/Sb(I)-SnO}_2 > \text{Ti/La-Sb(I)-SnO}_2 > \text{Ti/Sb(II)-SnO}_2 > \text{Ti/Co-Sb(I)-SnO}_2$ . For  $\text{Ti/Sb(I)-SnO}_2$  electrode and  $\text{Ti/Sb(II)-SnO}_2$  electrode, it is easy to understand that the concentration of oxygen vacancies in  $\text{SnO}_2$  crystal lattice decreased with increasing of Sb atoms, as the higher valence of  $\text{Sb}^{5+}$  needs more oxygen atoms to make charge balance when  $\text{Sn}^{4+}$  atoms in crystal lattice are replaced. While, this explanation could not be the same with the other two electrodes since neither  $\text{La}^{3+}$  nor  $\text{Co}^{2+}$  (or  $\text{Co}^{3+}$ ) cations has higher valence than  $\text{Sn}^{4+}$ . So, the simple mechanism is not enough and some complementary work should be considered. It is generally agreed that there exists an optimal doping amount for each doping species, less or more than this value might lead to decline of a certain property. The weakening of EPR intensity for  $\text{Ti/La-Sb(I)-SnO}_2$  electrode and  $\text{Ti/Co-Sb(I)-SnO}_2$  electrode might be due to an improper doping amount. Additionally, the discrepancy between different doping species should not be neglected. For example, as a kind of rare earths element, the radius of  $\text{La}^{3+}$  cation (106 pm) is much larger than that of  $\text{Sn}^{4+}$  cation (74 pm), it seems to be some difficult for La atoms to fill in the  $\text{SnO}_2$  crystal lattice or replace some Sn atoms. While, some researchers have found that the larger rare earths atoms can squash in

TABLE I EPR relative intensity of different samples

| Samples                | Ti/Sb(I)-<br>SnO <sub>2</sub> | Ti/Sb(II)-<br>SnO <sub>2</sub> | Ti/La-Sb(I)-<br>Sn <sub>2</sub> | Ti/Co-<br>Sb(I)-SnO <sub>2</sub> |
|------------------------|-------------------------------|--------------------------------|---------------------------------|----------------------------------|
| EPR relative intensity | 14.6                          | 6.2                            | 8.7                             | 1.0                              |

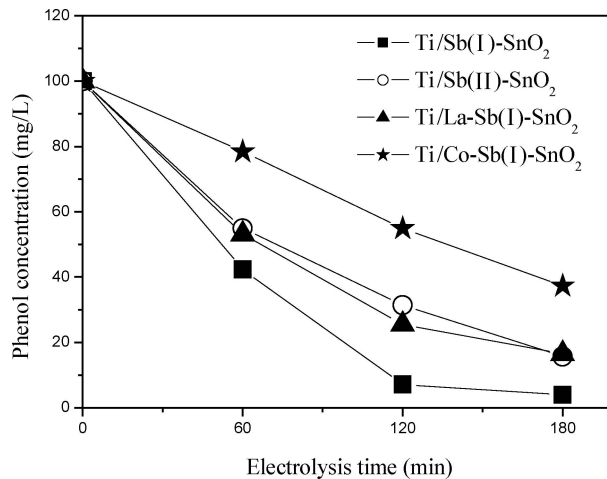


Figure 2 Electrochemical degradation of phenol with different electrodes as a function of electrolysis time.

another kind of smaller metal oxide crystal lattice and substitutes the inherent metal atoms under certain situations [9]. Therefore, the status is more complicated for the two kinds of quaternary metal oxide electrodes than that of ternary electrodes only with Sb doping species. More details should be investigated in the future.

Taking phenol as model substrate, the electro-catalytic performances of these four Sb doped Ti-base  $\text{SnO}_2$  anodes were investigated, as shown in Fig. 2. The electro-catalytic efficiency toward phenol degradation lies in the order  $\text{Ti/Sb(I)-SnO}_2 > \text{Ti/La-Sb(I)-SnO}_2 \approx \text{Ti/Sb(II)-SnO}_2 > \text{Ti/Co-Sb(I)-SnO}_2$ , which is matching with the EPR relative intensity order, imply that there might be some inherent relation between oxygen vacancy and electro-catalytic ability of Sb doped Ti-base  $\text{SnO}_2$  anode. In EC process, it is supposed that the hydroxyl radicals generated from water electrolysis, play a critical role in the EC oxidation mechanism of organic substances [10, 11]. Cominellis also suggests [10] that possible oxygen transition may occur from adsorbed hydroxyl radicals ( $\text{MO}_x\cdot\text{OH}$ ) to the lattice of the metal oxide anode forming the higher oxide  $\text{MO}_{x+1}$ , and both the two oxygen forms can oxidize organic substance with different efficiency. Obviously, oxygen vacancies should take part in this oxygen atom adsorption and transfer process and then influence the hydroxyl radical amount on the surface of oxide anode. According to our present experiments, the concentration of oxygen vacancies on  $\text{SnO}_2$  anode's surface is likely to influence the anode's performance toward phenol degradation which is agreed with the above hypothesis. Furthermore, the present experiments prove that introducing different foreign atoms can change the concentration of oxygen vacancies, and then, change the anode's catalytic ability.

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