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Experimental study and theoretical calculation on the conductivity and stability of praseodymium doped tin oxide electrode

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ABSTRACT

Ti/SnO_2-Sb_2O_4-Pr_2O_3/PbO_2 anodes are prepared by electrodepositing method. The electrodes are characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The degradation of phenol experiment and accelerated life test of the electrode are carried out. Futhermore, the formation energy, band structure and density of states (DOS) are calculated by first principles calculations. The results show that Pr doping can change the phase of SnO_2 and prevent the spread of the oxygen to the substrate, lower the interfacial resistance. The catalytic degradation of phenol rate is 58.3% when the doping ratio is 100:8. The service life of electrode reaches the maximum of 121 hours under a high current density of 4 A cm^{-2} in 1 mol L^{-1} of H_2SO_4 solution at 60 °C when the doping ratio is 100:8. Moreover, at the same doping ratio, the formation energy and band gap reach the minimums of -15.59 eV and 0.656 eV respectively. The experiments are consistent well with the theories. Thus, we conclude that the praseodymium doped tin oxide electrode is one promising acid-proof anode.

1. Introduction

Ti-based oxide electrode has been widely used in electrochemical industry, such as treatment of industrial wastewater containing toxic or non-biodegradable compounds for their low-volume requirements and environmental compatibility [1] and preparation for Li-ion batteries due to its high safety and excellent cycling stability [2]. However, it still exists some problems. The main problem is that reactive oxygen generating from anode will oxidize Ti substrates to non-conductive TiO_2, thus its conductivity is reduced. Many methods have been tried to solve this problem. So far, the best way is to add middle layer onto the Ti substrate surface, and there has existed tremendous relative reports [3,4]. Semiconductor metal oxides are used in many aspects due to their various advantages, such as photochemical activity [5,6] and degradation of organics [7]. As one promising acid-resistant material in strongly acidic solution, they are used as the middle layer to coat the Ti substrate surface. But in actual application, the middle layer is easy to peel off, thus, the service life of the electrode reduce. In order to solve this problem, people try to dope elements to form solid solution [8]. This is because for the metal oxide electrodes, the electro-catalytic properties are influenced by the chemical composition, the electronic structure and crystallinity of the oxide middle layers, and the morphology of the oxide middle layer. Doping other metal ions into the oxides can enhance the electro-catalytic activity and chemical or mechanical stability of oxide electrode. The following results show that the doping really can enhance the viscous force of the middle layer with Ti substrates surface and promote the performance of the electrode. Sumanta et al. [9] synthesized Pt doped SnO_2 thin films on TCO (transparent conducting oxide) substrates, and it was used as electrode to oxidize methanol, the study revealed that Pt-SnO_2 electrode is more effective for methanol electro-oxidization than pure SnO_2. Shekarchizade et al. [10] prepared Ti/SnO_2-Sb-Ni electrodes with various Ni- and Sb-doping levels by dip-coating thermal pyrolysis procedure, the results showed that the presence of appropriate amounts of Ni and Sb can improve the electrode performance, such as EOP activity, resistance, capacitance, roughness factor and service life. Dong et al. [11] studied the conductivity and stability of Bi-doped SnO_2 electrode using electrochemical method and first principle calculation, it turned out that the conductivity and stability of Bi-doped SnO_2 electrode reached best when the doping ratio is 100:8. Thereout, we can see that the study on doping of oxide coating has become research hotspot in recent years. Although people have made a lot of research about M(metal)-SnO_2 electrodes [12–14], however, there is no relative report on Pr-doped SnO_2 electrode whether using the experimental methods or theoretical calculations. Pr-doped SnO_2 electrode, as one strong

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acid-resistant anode material, has important significance for the development of electrochemical industry.

The purpose of this article is to systematically study the effect of Pr doping on the structural properties, conductivity and stability of SnO_2 by combining experimental methods with theoretical calculations.

2. Experimental

2.1. Pretreatment of Ti substrates

Ti substrates (80 mm × 10 mm × 2 mm) were burnished using abrasive paper, and then surface-treated at 80∼100 °C for 2∼3 h in 10% (quality ratio) NaOH solution. Subsequently, Ti substrates were placed into 10% hydrochloric acid solution for 4 h. The treated Ti substrates were cleaned using distilled water, after that they were stored in absolute ethyl alcohol to avoid contacting with air oxidation.

2.2. Preparation of Ti/SnO_2-Sb_2O_4-Pr_2O_3/PbO_2 electrode

The preparation process of Ti/SnO_2-Sb_2O_4-Pr_2O_3/PbO_2 electrode mainly included two steps: the preparation of middle layer and that of active layer. The schematic preparation process of Ti/SnO_2-Sb_2O_4-Pr_2O_3/PbO_2 electrode has been shown in Fig. 1. Firstly, the $SnCl_4 \cdot 5H_2O$, $SbCl_3$ and certain proportions of Pr were mixed together in n-butyl alcohol and hydrochloric acid mixed solution [11]. The solution was then coated uniformly on the prepared Ti substrate surface, and the substrate was dried for 10 min in a draught drying cabinet at 80∼100 °C. Subsequently, it was annealed for 10 min at 450 °C and then removed and cooled naturally. These steps were repeated 5 times, and the final sintering cycle lasted for 1 h at 550 °C. The middle layer was ready in the end. The Ti based SnO_2 electrode was prepared at the same time as a control group. Secondly, the as-prepared electrode was regarded as the anode, and the same Ti plate was considered as the cathode. Anodic electrodeposition of PbO_2 was performed on the surface of the prepared middle layer electrode at a constant current of 12.5 mA cm^{-2} in an electrolyte solution containing 0.1 mol L^{-1} HNO_3, 0.5 mol L^{-1} $Pb(NO_3)_2$, and 40 mmol L^{-1} NaF (additive). The Ti/SnO_2-Sb_2O_4-Pr_2O_3/PbO_2 electrode was well fabricated after 6 h of deposition. The as-prepared electrode was cleaned by distilled water and dried naturally in air room temperature.

2.3. Characterization

The X-ray diffraction (XRD) analysis of the sample was carried out using D/max-2500 diffractometer at a voltage of 40 kV and a current of 100 mA with Cu-Kα radiation across a 2θ range 20°−70°, at a scan rate of 8° (2θ) min^{-1}.

The scanning electron microscope (SEM) images were acquired using a JEOL JEM-2100 instrument working at an acceleration voltage of 10 kV.

2.4. Degradation of phenol

Electrochemical performance measurement was evaluated through the degradation of 50 mg L^{-1} phenol in water. The as-prepared electrode (1 cm × 4 cm) was regarded as the anode, and the same Cu plate was considered as the cathode. The distance between the two electrodes was 25 mm. The phenol concentration was taken every 15 min, with a current of 0.01 A.

2.5. Accelerated life test

An excellent electrode must be able to work efficiently for several years. However, testing of electrode stability under normal conditions is time consuming. To reduce the test time, we employed the accelerated life test under a high current density of 4 A cm^{-2} in 1 mol L^{-1} of H_2SO_4 solution at 60 °C. Similarly, the

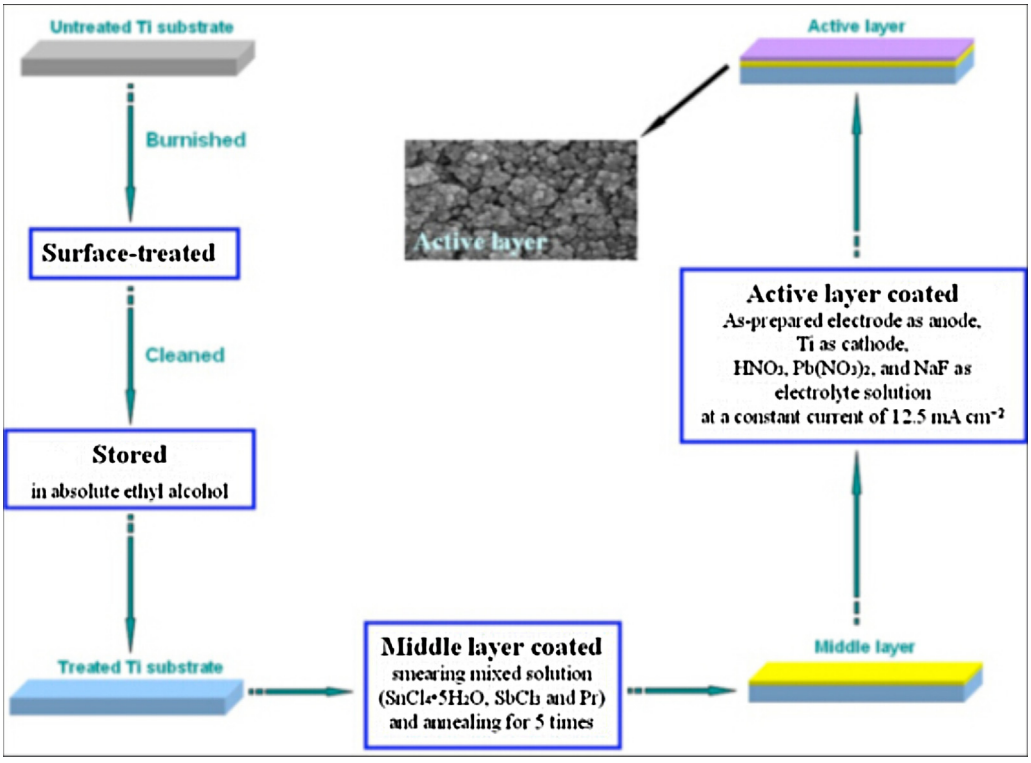

Fig. 1. Schematic illustration of preparation process for Pr-doped SnO_2 electrode.