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Effects of nickel doping on the preferred orientation and oxidation potential of Ti/Sb–SnO_2 anodes prepared by spray pyrolysis

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ABSTRACT

Nickel and antimony co-doped Ti/SnO_2 (Ti/Ni–Sb–SnO_2) anodes were prepared by spray pyrolysis. Effects of nickel concentration on the structure and onset potential for oxygen evolution of Ti/Ni–Sb–SnO_2 anodes have been systematically investigated. XRD analyses suggest that SnO_2 thin films grow in preferential orientation along (101) plane as the nickel concentration increases. The enhanced onset potential of oxygen is above 2.4 V vs NHE due to the introduction of nickel doping, and increases slightly with the nickel concentration. The calculated results show that work function of Ni/Sb co-doped SnO_2 also increases with the Ni doping level, which contributes to the enhancement of onset potential for oxygen evolution.

1. Introduction

Electrochemical advanced oxidation processes (EAOPs) to treat polluted waters have been increasingly attracted in recent years because they are the versatile and capable of removing a wide range of organic contaminants [1,2]. The anode materials play an important role on the efficiency of electrochemical advanced oxidation processes. Mixed metal oxide (MMO) electrodes, known as dimensionally stable anodes (DSA), are promising electrodes due to the high catalytic activity and contribution towards energy saving [3]. They consist of high corrosion-resistant materials such as RuO_2 [4], IrO_2 [5], PbO_2 [6] and SnO_2 [7]. The RuO_2-based and IrO_2-based anodes which are very expensive and have a low overpotential for O_2 evolution [8,9] slow down the development of electrochemical treatment in spite of their long service life. PbO_2-based anodes will introduce the toxic element Pb into the water during the electrochemical advanced oxidation processes.

Because of the low cost, nontoxic materials and high onset potential for oxygen evolution, SnO_2-based anodes are viewed as most promising anodes and intensively investigated [10–14]. But the short service life of SnO_2-based anodes is the biggest drawback for their application. Interlayer insertion and noble ion-doping can significantly improve the service life of SnO_2-based anodes [15–17] but will lead to the decreases in onset potential for oxygen evolution and increases of the cost of SnO_2-based anodes. Recently, it is found that Ni/Sb co-doping significantly enhanced the accelerated lifetime of SnO_2 anode but did not decrease the onset potential for oxygen evolution [10,18,19]. Moreover, the Ni/Sb-SnO_2 anodes has the novel capability of generating ozone with efficiencies >20% at room temperature [19–21]. Therefore, the Ni/Sb co-doped SnO_2 anodes have great potential in EAOPs and electrochemical ozone production.

Currently, the spray pyrolysis for deposition of SnO_2 thin films has gained growing attention because the doped SnO_2 thin films prepared by spray pyrolysis are compact [22–24]. The Ti/Sb–SnO_2 anodes prepared by spray pyrolysis [25] have less cracks than those fabricated by spin coating [26] and dip coating [7,27]. Those cracks have greatly negative effects on the service life of SnO_2 anodes [28]. So, the spray pyrolysis for deposition of SnO_2 thin films can benefit the service life of SnO_2-based anodes. Comninellis et al. [29] fabricated the SnO_2 anodes using spray pyrolysis method with the precursor solution flow and carrier gas flow of 1.86 and 3 cm^3 min^{-1}, respectively. They exhibited longer service lifetime than the conventional Ti/Sb–SnO_2 anodes [16]. However, to our knowledge, the Ni/Sb co-doped SnO_2 anodes generally are fabricated by dipcoating method [10,30,31]. There is no reports on the

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fabrication of Ni/Sb co-doped SnO_2 by the spray pyrolysis. Moreover, there are few works that systematically investigate the effects of Ni concentration on the crystal structure and electrocatalytic properties of Ti/Ni–Sb–SnO_2 anodes.

In the present work, we demonstrate the synthesis of Ni/Sb doped SnO_2-based anodes and seak to investigate the influences of Ni concentration on the onset potential for oxygen evolution and the crystalline structure of Ti/Ni–Sb–SnO_2 anodes. It is found that the Ti/Ni–Sb–SnO_2 anodes exhibit enhanced onset potential for oxygen evolution of above 2.4 V vs NHE, closed to the onset potential (2.7 V) of BDD [32,33]. The work functions of the SnO_2 with different Ni concentrations are calculated using the first-principle based on density functional theory (DFT) to explore the reasons for the enhancement in the onset potential for oxygen evolution.

2. Experiment details and calculation methods

The Ti/Ni–Sb–SnO_2 anodes were prepared by spray pyrolysis [34,35] on Ti substrate which is pretreated by sandblasting, then ethced in boiling 10% oxalic acid during 30 min. 1.0 g $SnCl_4 \cdot 5H_2O$ and 0.1 g $SbCl_3$ were dissolved into 50 ml ethanol and 5 ml HCl mixture. Then, the required amount of $NiCl_2 \cdot 6H_2O$ was added to the spray solution to obtain 2.5, 7.1, 9.2 and 11.3 at.% Ni doping in the precursor solution. The height between the spray nozzle and the hot plate was 3 cm and the flow rate of carrier gas (air) was 100 L/h. The Ti substrates were put on the heating plate of which temperature was controlled by temperature controller. Before deposition of SnO_2 films, the temperature of Ti substrates was measured by temperature meter.

The cyclic voltammetry (CV) experiments were carried out in 0.5 M H_2SO_4 solution using a standard three electrode cell, Pt plate with the area of 1×1 cm^2 was used as a counter electrode and Hg/$Hg_2SO_4 \cdot K_2SO_4$ (0.64 V vs NHE) as a reference electrode. The fabricated Ti/Ni–Sb–SnO_2 anodes were used as the working electrode.

The surface morphologies of Ti/Ni–Sb–SnO_2 anodes prepared using the precursor solution containing 2.5, 7.1, 9.2 and 11.3 at.% Ni were observed by scanning electron microscopy (HITACHI S4800). The crystal structure analysis of prepared Ti/Ni–Sb–SnO_2 anodes were carried out using the x-ray Diffraction (XRD) technique. The diffractometer was used employing $Cu_{K\alpha}$ radiation, with a scanning angle (2θ) range of 10°–54°.

The calculations based on the density functional theory were performed using the Quantum ESPRESSO package [36], the exchange-correlation energy of interacting electrons was treated by using the Perdew-Burke-Ernzerhof generalized gradient approximation [37]. All the models were calculated with a Monkhorst-Pack k-point ($4 \times 5 \times 1$).

3. Results and analyses

In order to obtain the optimized deposition temperature, the Sb doped SnO_2 thin films are deposited at different temperature from ~377 to ~550 °C. Fig 1 shows the scanning electron microscopy (SEM) images of as-deposited Ti/Sb–SnO_2 electrodes at different deposition temperature. As can be seen, there are no typical cracks of the SnO_2 coatings prepared by thermal decomposition [7,26] and all of SnO_2 thin films are compact. The SnO_2 crystal particles have small size of about 500 nm at low temperature of 377 ± 5 °C (Fig. 1a). As the deposition temperature increase, the average particle size of SnO_2 increase. The average size of SnO_2 crystal particles becomes large at high temperature of 550 ± 5 °C (Fig. 1d). It is about 2 μm. The element distribution of Sn, Sb and O as shown in Fig. 2 illustrates the homogeneity of the Ti/Sb–SnO_2. Consequently, we chose the deposition temperature of 550 ± 5 °C to prepare the Ti/Ni–Sb–SnO_2 electrodes with different Ni concentration due to the large SnO_2 crystal particles which leads to a good durability [10].

In order to investigate the effects of Ni concentration on the crystal structure and electrocatalytic properties of Ti/Ni–Sb–SnO_2 anodes, it would be desirable to have an elemental characterization. We attempted to detect and quantify the Ni content in our anodes by X-ray analyses (EDX) and X-ray photoelectron spectroscopy (XPS), but unfortunately it has not possible to obtain

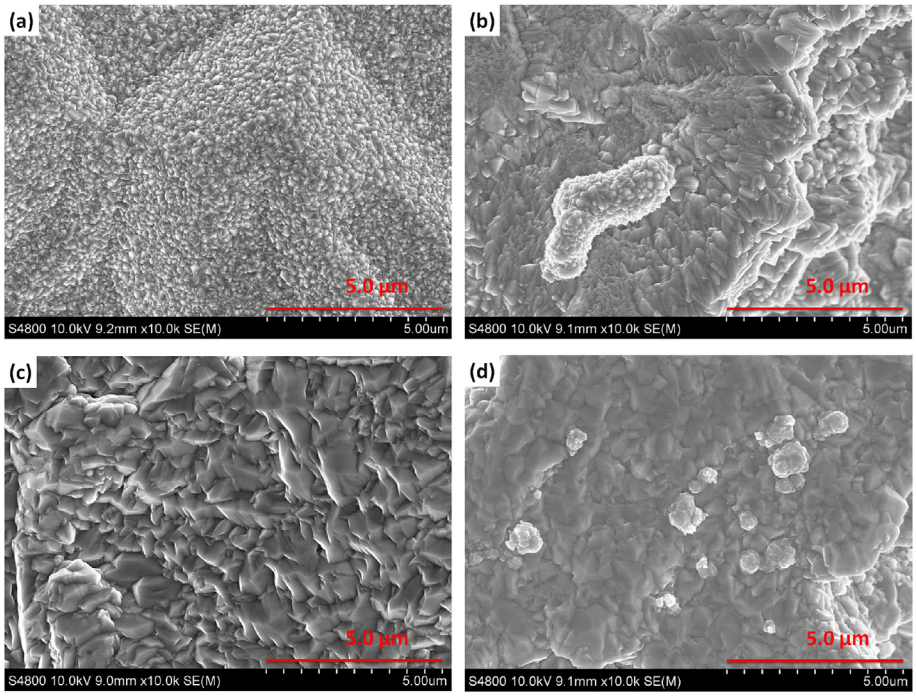

Fig. 1. SEM images of the Ti/Sb–SnO_2 electrodes deposited at temperature of (a) 377 °C, (b) 417 °C, (c) 510 °C and (d) 550 °C. Magnification: 10,000 ×.