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Preparation and Characterization of a Pd modified Ti/SnO_2-Sb anode and its electrochemical degradation of Ni-EDTA

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ABSTRACT

An optimized metal oxide electrode (Ti/SnO_2-Sb-Pd) was prepared via thermal decomposition and used in the electrochemical degradation of Ni-EDTA. The electrode was characterized by SEM, XRD, XPS, and electrochemical characterizations including linear-sweep voltammetry (LSV), cyclic voltammetry (CV) and chronopotentiometry (CP) techniques. It was found that Pd doping could effectively change the surface morphology and lattice parameters of the metal oxide electrode. Pd can facilitate the entry of more Sb into SnO_2 crystals and promote the reduction of Sb from the +5 to the +3 state. The interaction of these metals raised the oxygen evolution potential (OEP) and electrochemical surface area of the electrode, in addition to reducing the degradation potential and increasing the degradation current of Ni-EDTA. When the molar ratio of Pd:Sn was 2.5%, the electrode could simultaneously degrade 87.5% of Ni-EDTA and recycle 17.9% of elemental Ni on the cathode within 120 min. At the same time, with Pd doping, the lifetime of the electrode was increased more than 40 times, demonstrating good potential for application in industry.

1. Introduction

Ethylenediaminetetraacetic acid (EDTA), a widely used chelating agent, has been applied in many industries for its outstanding complexation capability. It has been ubiquitously detected over a wide range of concentrations in many surface and drinking waters [1]. Because of its strong chelating ability and stability with many heavy metal ions, e.g., Cr [1], Pb, Zn, Cd [2–4], Cu [5,6], and Ni [7], EDTA plays an extremely important role in the electroplating process. On the other hand, it is very difficult to remove these metal-EDTA complexes by conventional chemical precipitation processes, leading to severe effects on the environment [8].

Many promising techniques have been developed to treat these metal-EDTA containing wastewaters, such as electrocoagulation [5,9], Fenton reaction-hydroxide precipitation (FR-HP) coupled with ultrasonic [10] or microwave [11] processes, photocatalytic oxidation [2,12,13], and immobilized cells [14]. However, some ineluctable shortages limit their practical applications in engineering, including the production of large amounts of sludge, addition of chemical agents, low energy utilization, complex reactor requirements, and long reaction times. Thus, there is an urgent need to explore a low cost and stable method to break the metal-EDTA complex effectively and increase the removal efficiency of metal ions.

Currently, electrochemical advanced oxidation processes (EAOPs) have attracted lots of attention for their high degradation efficiency, versatility, convenience, and flexibility. The choice of anode materials is crucial for EAOPs. Mixed metal oxide (MMO) electrodes, especially dimensionally stable anodes (DSA), have been studied frequently and used to mineralize organic pollutants due to their high catalytic activities. Titanium substrates coated with different metal oxides, including RuO_2 [15–18], IrO_2 [18–21], PbO_2 [22] and SnO_2-Sb [23,24], exhibited favourable catalytic oxidation performance. However, RuO_2 and IrO_2 anodes are expensive, and PbO_2 anodes introduce Pb into water, making them less than ideal anodes for practical applications.

In the area of DSA materials, the Sb-doped Ti/SnO_2 anode is regarded as one of the most promising anodes due to its low cost, nontoxicity and high oxygen evolution potential (OEP) [25,26]. Li

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et al. compared Ti/SnO_2-Sb, Ti/RuO_2, and Pt as anodes to degrade phenol and found that the Ti/SnO_2-Sb electrode showed more apparent catalytic activity for rapid organic oxidation [27].

Although Sb-doped SnO_2 anodes are often short-lived due to anodic polarization in acidic media, noble ion doping can remedy this drawback and extend their service life. Berenguer found that incorporating a small amount (approximately 3%) of both Pt and Ru into SnO_2– Sb-doped electrodes produced a 400 fold increase in their service life [28]. Other Sb-doped SnO_2 anodes, such as Ti/SnO_2-Sb/TiN [29], Ti/SnO_2-Sb/Nb-PbO_2 [30], Ti/SnO_2-Sb/Cu-NRs [31], and Ti/SnO_2-Sb/Ce-PbO_2 [32], also showed considerable catalytic oxidation performance for organic pollutants.

As an excellent catalytic material, elemental palladium has exhibited its unique catalytic activity in many reactions. Freakley et al. [33] found that Pd-Sn catalysts could directly generate H_2O_2, which can oxidize the vast majority of organic substances. Du et al. prepared a Ti/TiO_2-RuO_x-PdO anode to decolorize an Active Orange 5R solution [16] and noted out that Pd could promote the electrooxidation process [34]. Because palladium and Sb-doped SnO_2 both have their own unique catalytic abilities, we were eager to combine them to make a Ti/SnO_2-Sb-Pd electrode, and then explore its crystal structure and electrocatalytic properties.

In this work, the thermal decomposition method was used to obtain a Pd-doped Ti/SnO_2-Sb electrode. To explore the influence of Pd doping on the Ti/SnO_2-Sb electrode, the surface morphology, crystal structure, and composition of the electrode were characterized by SEM, EDS, XRD, and XPS. Additionally, its electrochemical capabilities were tested by cyclic voltammetry (CV), linear sweep voltammetry (LSV) and chronopotentiometry (CP). The electrode was then used for the oxidation of Ni-EDTA containing wastewater, where it showed excellent- electrochemical degradation ability. Finally, accelerated lifetime tests were performed to validate the electrode's application potential in industry.

2. Experimental

2.1. Materials and reagents

Titanium plates (purity >99%) with dimensions of 20 × 20 × 1 mm were purchased from Dongguan Huitai Co. Ltd. (Dongguan, China). The $SnCl_4 \cdot 5H_2O$, $SbCl_3$, and $PdCl_2$ were purchased from Aladdin (Shanghai, China). All reagents were of analytical grade and were used without further purification. Ni–EDTA solution was prepared by mixing an equal molar ratio of $NiCl_2 \cdot 6H_2O$ and $Na_2EDTA \cdot 2H_2O$. 0.1 M HCl and 0.1 M NaOH were used to adjust the pH of the Ni–EDTA solutions. Distilled water was obtained from a Millipore-Q system and used throughout the work.

2.2. Electrode preparation

2.2.1. Titanium surface treatment

Before the experiment, the titanium substrate was pretreated to form a uniform and active structure for metal oxide adhesion. First, the sheets were polished by 240-grit and 800-grit abrasive bands successively to remove the oxide surface. Then, they were soaked in 40% sodium hydroxide solution at 80 °C for 3 h to remove grease from the surface. Next, the sheets were etched in 15% oxalic acid solution at 95 °C for 3 h after rinsing with water. Lastly, they were ultrasonically cleaned with acetone for 15 min. These sheets lost their metallic lustre and obtained a grey surface with a uniform roughness. They were stored in ethyl alcohol until further use.

2.2.2. Coating metal ions

For the preparation of precursor solution, 28.05 g of $SnCl_4 \cdot 5H_2O$, 1.64 g of $SbCl_3$, and a certain amount of $PdCl_2$ (Pd/Sn molar ratios of 0, 1.5:100, 2:100, 2.5:100, 3:100, and 3.5:100, respectively) were dissolved in 50 mL of isopropanol. Then, 5 mL of concentrated (37%) HCl was added and stirred to promote dissolution, and then the solution was diluted to 100 mL with isopropanol. Afterwards, the obtained precursor solution was brushed onto a pretreated Ti plate evenly, dried at 150 °C for 10 min, and then calcined at 550 °C for 10 min in a muffle furnace. After naturally cooling to room temperature, the sheets were brushed again. This brushing-drying- calcining- cooling procedure was repeated 15 times, and the final calcination step was allowed to proceed for 1 h.

2.3. Analytical procedures

The surface morphology and structure of the synthetic electrodes were investigated using a scanning electron microscope (SEM, ZEISS Merlin, Germany) equipped with an energy dispersive spectrometer (EDS) and X-ray diffraction (XRD, Bruker-D8 ADVANCE, Germany), where the samples were exposed to X-ray ($k = 1.5418$ Å) with the 2θ angle varying between 10° and 90° with Cu $K\alpha$ radiation. The crystalline size and the lattice parameters were determined from XRD data by MDI Jade 6, with PDF standard card as a reference. X-ray photoelectron spectroscopy (XPS) data were recorded with the Al $K\alpha$ line at 15 kV and 51 W (PHI X-tool, DE), and the binding energies were calibrated with respect to the signal of contamination carbon (284.8 eV).

Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and chronopotentiometry (CP) were measured on a CHI-660b electrochemical workstation (Shanghai Chenhua Instruments Co. Ltd., China). The modified Ti substrate was used as the anode, a carbon electrode was used as the counter electrode, and a saturated calomel electrode (SCE, Hg/Hg_2Cl_2/KCl, 0.2415 V vs NHE) was employed as the reference electrode. The electrolyte volume was 100 mL with a certain concentration of Na_2SO_4 or H_2SO_4 solution as the electrolyte.

The concentration of Ni-EDTA was determined using a high-performance liquid chromatography (HPLC) system consisting of a 2695 reparation module and a 2998 photodiode array detector (Agilent Technology). An Agilent Eclipse C-18 column (4.6 × 250 mm, 5 μm) was used as the separation column for Ni-EDTA and the intermediates. The determination conditions had been optimized before; thus, the mobile phase consisted of 75:25 (v:v) phosphate buffer salt: acetonitrile at a flow rate of 1 mL min^{-1} and a column temperature of 25 °C. The buffer salt solvent was composed of 20 mM ammonium phosphate, and pH was adjusted to 2.5 using phosphoric acid. The detection wavelength was 210 nm. The concentration of Ni was determined by atomic absorption spectroscopy (AAS, Pin AAcle 900T, Perkin Elmer, USA).

2.4. Electrochemical oxidation of Ni-EDTA

The electrochemical oxidation procedure for Ni-EDTA was carried out in a 200- mL beaker with a two- electrode system (the modified anode and a fresh Ti sheet cathode with a 1-cm interval). The solution volume was 100 mL, the initial Ni-EDTA concentration was 0.1 mM, 0.1 M Na_2SO_4 was used as the electrolyte, and the pH was adjusted to 3.0. The current was kept at 30 mA (10 mA cm^{-2}) immutably, and the reaction time was 120 min.

3. Results and discussion

3.1. Characterization of Ti/SnO_2-Sb-Pd electrodes

3.1.1. SEM characterization

The morphology and structure of the electrodes obtained are shown in Fig. 1. It was observed that the thermal decomposition method produced a typical kind of cracked-mud structure on the Ti sheet surface, which was attributed to the alternation of high and