



Fabrication of Ti/Ti-V-Sn-Sb-oxide electrode with improved electrocatalytic activity towards organic degradation

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Abstract

In this work, a composite metal oxide electrocatalyst was developed to remove the organic pollutants through an electrochemical advanced oxidation process (E-AOP) while examining the effect of current density. Namely, Ti/Ti-V-Sn-Sb-oxide coated electrocatalyst was successfully prepared using dip coating method. The removal efficiency has been determined from the anodic oxidation treatment of 100 mL Methyl Orange (MO) azo dye solution in 0.05 mol L⁻¹ Na₂SO₄ at pH 3 at different current densities of 10, 20, 30, 40 mA cm⁻². The decolorization rate were about 96.45% for degrading 50 mg L⁻¹ MO at the optimal current density of 30 mA/cm⁻² and treatment duration of 60 min. The promising electrocatalytic performance of Ti/Ti-V-Sn-Sb-oxide electrocatalyst render the respective anode as a low-cost dimensionally stable anode (DSA) for decomposition of organic pollutants in the aqueous solution.

Keywords: Electrocatalytic degradation, dip coating, Methyl orange, Wastewater treatment.

Introduction

Nowadays, Environmental pollution is considered as a major problem worldwide. In particular, the risks and damages caused by refractory organic pollutants, have drawn growing concern in the past decade. One big category of organic pollutant is dyestuff, which is extensively present in effluents of textile, paper, leather, cosmetics and other industries [1]. Such wastewaters might cause serious environmental health problems mainly due to their toxicity and potential hazardous health effects (carcinogenicity, mutagenicity and bactericidal) on living organisms, including human beings. Traditional wastewater treatment methods, including physical, chemical and biological processes have so far failed to meet stringent standards for the removal of such pollutants, and therefore a number of alternative technologies have been investigated [2,3,4].

There is an increasing interest in the study of the destruction of organic pollutants from wastewaters by means of anodic oxidation (AO). AO can be applied to wastewaters with high chemical oxygen demand (COD) and total organic carbon (TOC), low biodegradability and toxic pollutants, working at intermediate temperatures. This environmentally friendly method is an electrochemical advanced oxidation process (E-AOP) based on oxidizing pollutants directly or through the formation of highly-oxidative active oxygen species such as hydroxyl radical (OH[•]) at the anode surface. This radical possesses a relatively high standard reduction



potential ($E^{\circ}(\text{OH}^{\bullet}/\text{H}_2\text{O})=2.80 \text{ V/SHE}$) with a very short half-life of 10^{-4} s which can react with organics in a non-selective manner through a full conversion into CO_2 and inorganic ions [5]. EAOP as a promising technology has been used in many different fields of environmental pollution treatments, which is due to their strong oxidation performance, easy implementation, and environmental compatibility [2]. Despite the high degradation efficiency, however, such processes are usually energy-intensive because of a high overpotential and competitive electrochemical side reactions occurring in an aqueous medium (such as oxygen evolution reaction (OER)). Therefore, a lot of researches have mainly focused on ways to improve the electro-catalytic activity and chemical stability of the anode materials, in order to improve treatment efficiency of contaminants. In this regard, dimensionally stable anodes (DSAs) have been well studied for organic matters removal depending on its capability to generate hydroxyl radicals, accompanied with oxygen evolution reaction (OER) [6,7,8]. The DSAs are composed of a metal substrate coated with an electro-catalytic layer. Ti, Ta, Zr, W, Nb and Bi are the typical substrates in which Ti as the most common substrate together with Pt, Ir and Ru as the electro-catalysts (coating layer), either pure or as metal oxides have been widely employed. Other metal oxides such as TiO_2 , Ta_2O_5 , ZrO_2 , Nb_2O_5 and SnO_2 are used as dispersing or stabilizing agents, and Sb is often added as a doping mediator [9].

It has been widely confirmed that generation of OH^{\bullet} and oxygen evolution are anodic competitive reactions, so higher oxygen evolution potential (OEP) of the electrode are needed in order to acquire higher OH^{\bullet} generation efficiency [10]. For this purpose, here, in this study, we aim to introduce vanadium as a new catalyst agent to combine with Ti/ SnO_2 - Sb_2O_5 -based DSAs to enhance the degradation efficiency of organic pollutants. Titanium was also added to the structure, in order to further improve the stability of this new proposed DSA. Scanning electronmicroscopy (SEM) and x-ray diffraction (XRD) were used to characterize the modified anode. The oxidation power of this anode was assessed taking methyl orange azo dye as the model pollutant. Methyl orange ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$) presents a red quinone-type structure in acidic medium and a yellow azo-type one under alkaline conditions. It is not biodegradable and possesses mutagenic properties [11]. The decolourization and mineralization of MO was investigated by UV-vis measurements.

Experimental Section

Metal oxide coatings were fabricated on $20\text{mm} \times 10\text{mm} \times 0.8\text{mm}$ flat titanium substrate using thermal decomposition method. The precursor solution was prepared by adding a certain concentration of the metal salt solution of antimony trichloride (SbCl_3 , 99+) and stannic chloride hydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 99+) in 1:1 (volume ratio) of hydrochloric acid (HCl, 37.0%) and isopropanol ($\text{C}_3\text{H}_8\text{O}$, 99.7%), to the solution of vanadium pentoxide (VP) (V_2O_5 , 99+) and titanium isopropoxide (TTIP) ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$) in hydrochloric acid (HCl, 37.0%). The proper amount of precursors were calculated, in each solution, to yield a coating with a relative molar compositions of interest for Ti:V:Sn:Sb. In order to form the metal oxide coating, dried Ti substrates were dip coated, with certain withdraw speed and immersion time. The one step coated substrate dried in an oven to evaporate the solvent, and then heated in an atmospheric pressure air furnace. This process was repeated to result in a desired coating thickness. At the end of the coating process, the resulting films were annealed to form the oxide phases.

MO ($\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$) was selected as a model dye wastewater. The MO degradation experiment was carried out in a 100 mL cylindrical vessel with a magnetic stirrer at room temperature. In the removal experiment, the working anodes was as described above, a



graphite rod with the almost 5 cm² area was employed as the cathode, at a electrode spacing of 10 mm. The dye solution containing MO was prepared by dissolving MO dye in 1 L of 0.05 M Na₂SO₄ (the initial concentration was 50 mg L⁻¹). pH values were adjusted by 0.5 M HCl to 3.

Results and discussion

The SEM micrograph of the as-prepared Ti-Sn-Sb-Oxide and Ti-V-Sn-Sb-oxide electrocatalysts are shown in Figure 1. It is observed that Ti-Sn-Sb-oxide has a quite uniform surface with wide and deep cracks, while adding vanadium to the structure results in the formation of a rough surface (Fig 1b). It is also well observed that the Ti-V-Sn-Sb-oxide electrocatalyst surface composed of two different structural textures. The first phase comprises the bottom compact layer and the second one consisted particles grown on the surface underneath. It can be concluded that the flower-like and homize vanadium particles (inset to Fig 1b) are homogeneously formed on the Ti-Sn-Sb-oxide film. This indicates that it could modify the coating morphology as it decreases the film compactness.

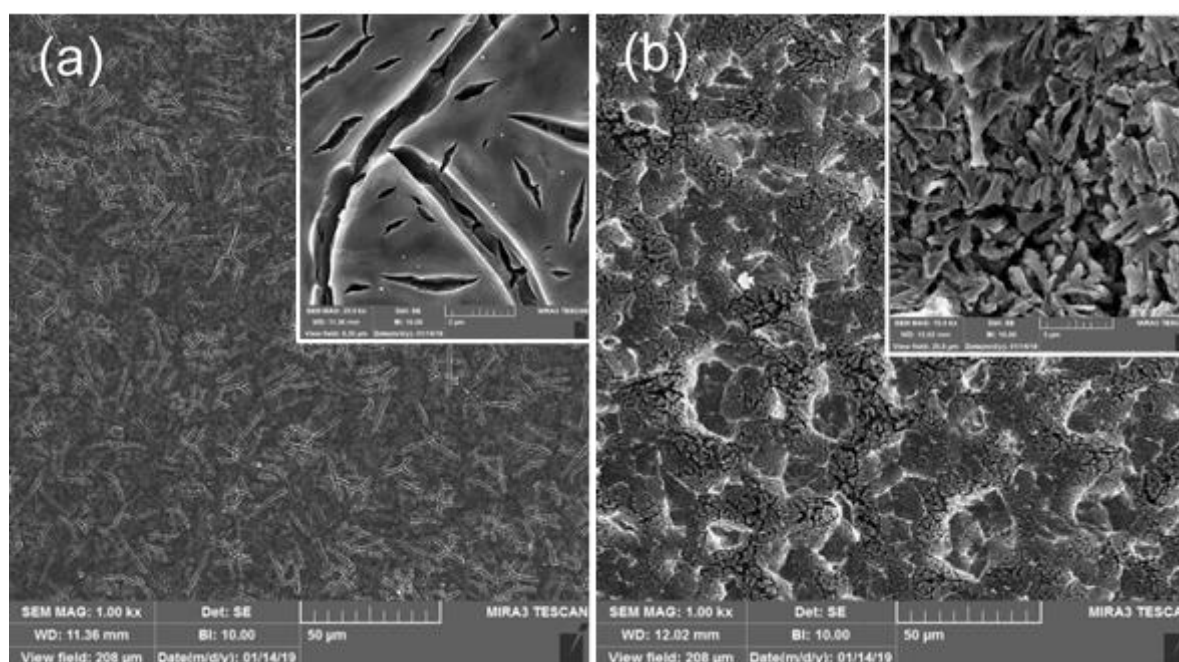


Fig. 1 SEM images of Ti/Ti-Sn-Sb-oxide (a), Ti/Ti-V-Sn-Sb-oxide electrodes (b)

Figure 2 represents the XRD pattern of synthesized electrocatalysts. Characteristic diffraction peak, for titanium oxide film, is related to anatase phase (JCDPS NO. 21-1272). Vanadium oxide film shows a VO₂ phase (JSPDS No. 43-1051) and a V₂O₅ phase (JSPDS No. 41-1426), after annealing. Given that most of the vanadium oxide film crystalline phases are related to VO₂, it can be concluded that dissolution of V₂O₅ in HCl, resulted in the reduction of vanadium from V(V) to V(IV). Furthermore, According to the XRD pattern of Ti/Ti-V-Sn-Sb-oxide, it can be seen that the dominant crystalline phase is also related to the VO₂. This point, together with the comparison of Ti/Ti-Sn-Sb-oxide and Ti/Ti-V-Sn-Sb-oxide XRD patterns can confirm the observations of Fig. 1b regarding the existence of two phases of Ti-Sn-Sb-oxide and vanadium particles on the Ti/Ti-V-Sn-Sb-oxide coated electrocatalyst surface.



In the electrochemical system, current density is an important parameter during the electrochemical oxidation process. The performance of the MO degradation was evaluated at various current densities ranging from 10 to 40 mA cm⁻². Fig. 3 illustrates the relationship between the removal rates of MO for different current densities. It can be seen that the MO removal efficiency increased with the increase of current density from 10 mA cm⁻² to 40 mA cm⁻².

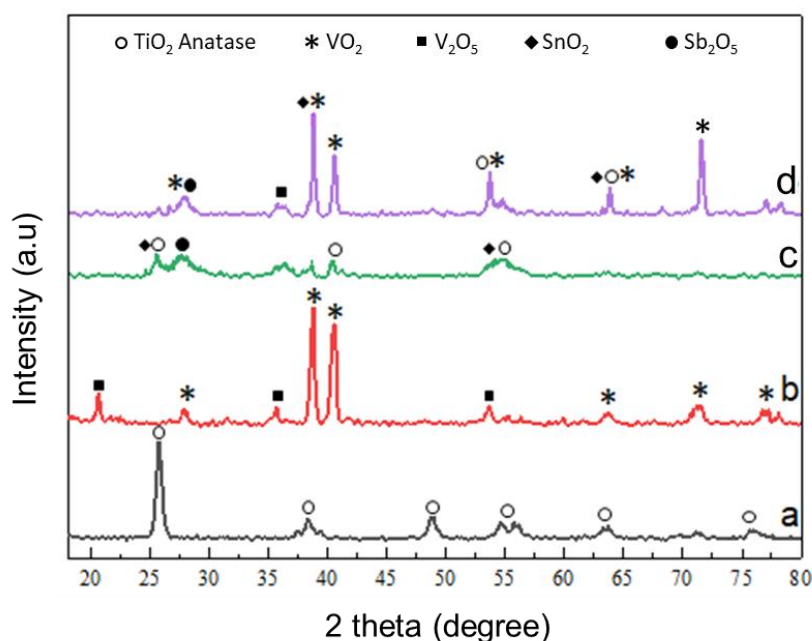


Fig. 2 XRD patterns of Ti/Ti-oxide (a), Ti/V-oxide (b), Ti/Ti-Sn-Sb-oxide (c) and Ti/Ti-V-Sn-Sb-oxide electrocatalysts.

However, removal efficiency drops at 40 mA cm⁻², after 20 minutes. This may be due to the degradation of coating at higher current densities. In addition, with the increase of current density, some undesirable side reactions, like electrolysis of water and oxygen evolution of OH, would compete with the electrochemical oxidation of the contaminants, which declines the current efficiency[2]. After 60 min of E-AOP, the MO removal efficiencies reach 83.8%, 97.5%, 99% and 96.45% at 10, 20, 30, 40 mA cm⁻², respectively. Therefore, in order to obtain optimal efficiency of degradation and better energy utilization, the optimal current density for the electrochemical degradation of MO is considered to be 30 mA cm⁻².

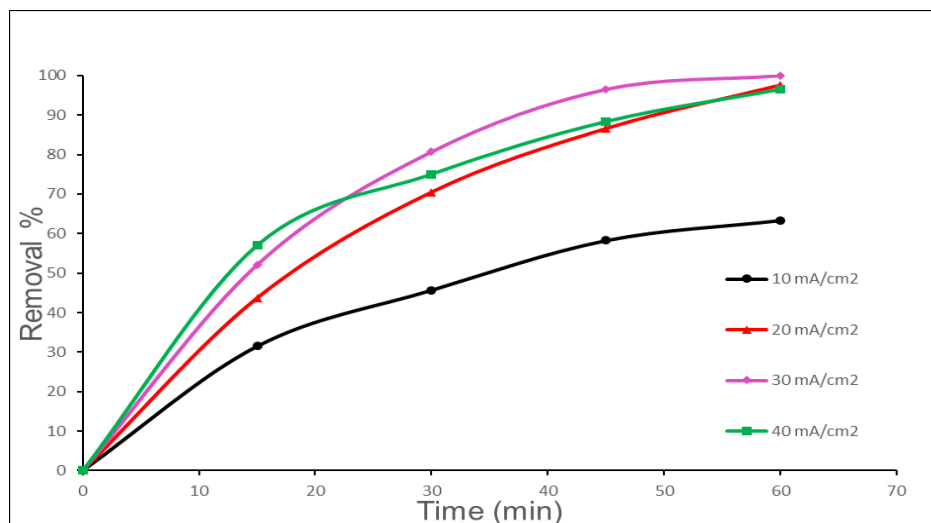


Fig. 3 The effect of current density on MO removal efficiency as a function of time

Conclusions

Titanium substrates were successfully coated with Sn, Sb, V and Ti oxides by the thermal decomposition method. SEM and XRD corroborated that the synthesized electrodes were mainly composed of a mixture of Ti-V-Sn-Sb oxides. The electro-catalytic oxidation of MO on Ti/Ti-V-Sn-Sb-oxide was examined at different current densities of 10 mA cm⁻² to 40 mA cm⁻². The 99% removal efficiency in less than 1 hour occurred at the optimal current density of 30 mA cm⁻².

References

- [1] Li, Shu-Hong, et al. "Electrochemical degradation of methyl orange on Pt-Bi/C nanostructured electrode by a square-wave potential method", *Electrochimica Acta*, 92, 93-101, (2013).
- [2] Xu, Mai, et al. "Fabrication of cerium doped Ti/nanoTiO₂/PbO₂ electrode with improved electrocatalytic activity and its application in organic degradation", *Electrochimica Acta*, 201, 240-250, (2016).
- [3] Francisca C. Moreira, Rui A.R. Boaventura, Enric Brillas, V'itor J.P. Vilar, "Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters", *Applied Catalysis B, Environmental* 31, 1-35, (2017).
- [4] Garcia-Segura, Sergi, and Enric Brillas. "Applied photoelectrocatalysis on the degradation of organic pollutants in wastewaters", *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 31, 1-35, (2017).
- [5] Isarain-Chávez, Eloy, et al. "Comparative electrochemical oxidation of methyl orange azo dye using Ti/Ir-Pb, Ti/Ir-Sn, Ti/Ru-Pb, Ti/Pt-Pd and Ti/RuO₂ anodes", *Electrochimica Acta*, 244, 199-208, (2017).
- [6] Yu, Han, et al. "Energy-saving removal of methyl orange in high salinity wastewater by electrochemical oxidation via a novel Ti/SnO₂-Sb anode—Air diffusion cathode system", *Catalysis Today*, 258, 156-161, (2015).
- [7] Sirés, Ignasi, et al. "Electrochemical advanced oxidation processes: today and tomorrow. A review", *Environmental Science and Pollution Research*, 21.14, 8336-8367, (2014).



- [8] Shao, Dan, et al. "High-performance Ti/Sb–SnO₂/Pb₃O₄ electrodes for chlorine evolution: Preparation and characteristics", *Journal of hazardous materials*, 267, 238-244, (2014).
- [9] X. Qin, F. Gao, G. Chen, "Effects of the geometry and operating temperature on the stability of Ti/IrO₂-SnO₂-Sb₂O₅ electrodes for O₂ evolution", *J. Appl. Electrochem.* 40, 1797–1805, (2010).
- [10] Aguilar, Zaira G., et al. "Ti| Ir–Sn–Sb oxide anode: Service life and role of the acid sites content during water oxidation to hydroxyl radicals", *Journal of Electroanalytical Chemistry*, 820, 82-88, (2018).
- [11] K.T. Chung, G.E. Fulk, A.W. Andrews, "Mutagenic testing of some commonly used dyes", *Appl. Environ. Microbiol*, 42, 641-648, (1981).