Effect of nickel doping on electrochemical ozone generation of nickel and antimony doped tin oxide anodes

Supandee Maneelok[1*] and Chontira Sangsubun[2]

[1] *Department of Occupational Health and Safety, Faculty of Health and Sports Science, Thaksin University, Phatthalung, THAILAND*

[2] *Department of Physics, Faculty of Science, Thaksin University, Phatthalung, THAILAND*

**Corresponding author; E-mail address: msupandee@tsu.ac.th*

Abstract

Ozonization has been recognized as a highly effective agent for water and wastewater treatment, therefore, it has been applied for disinfection, oxidation of organic and inorganic compound, and destruction of microorganisms. Ozone can be generated by electrochemical process using the nickel and antimony doped tin oxide (NATO) catalyst. This study presents the optimal Ni content of NATO and their surface properties to correlate with ozone generation. The NATO anodes were prepared by sol-gel and dip-coating method with varying the Ni content between 0.5% and 3% with calcination temperature at 450 °C. The significant findings show that XRD pattern of all NATO anodes showed a single rutile phase, resulting Sb^{5+} and Ni^{2+} ions replaced into Sn^{4+} ions in the SnO_2 lattice due to the ion radius. The morphology of NATO anodes demonstrated spherical shape and well disperse. Regarding the chemical oxidation state from XPS technique, the binding energies of the $Sb3d_{3/2}$ peak at 540.61 eV and 541.49 eV agree with Sb^{3+} and Sb^{5+}, respectively. These chemical oxidation state can drive to active sites of oxygen adsorption and ozone activity. The optimal Ni content at 1.5% on the NATO anode was obtained the maximum ozone current efficiency of 18.7% and the current density ca. 0.08 A cm^{-2} in 0.5 M H_2SO_4 with potential of 2.7V. The ozone current efficiency and current density decreased as a function of nickel content. An electrochemical oxidation rate is observed at high current densities due to production of •OH and O_3.

Keywords: Ozone, Electrochemical, Nickel and antimony doped tin oxide

1. Introduction

Electrochemical ozone generation is a process that involves the production of ozone through the use of electricity. Ozone is a powerful oxidizing agent that is commonly used in various industries, including water and waste water treatment, air purification, and food processing, due to its ability to destroy bacteria, viruses, and other contaminants. Moreover, it can be used to oxidize and destroy pollutants in the air, such as volatile organic compounds (VOCs) and odors [1-2]. The principle of electrochemical ozone generation is the electrolysis of water. Molecule of water consists of two hydrogen atoms and one oxygen atom, and it can be split into its component parts through the application of an electrical current. When an electrical current is passed through water, the hydrogen atoms are attracted to the negatively charged electrode, while the oxygen atoms are attracted to the positively charged electrode. This results in the production of oxygen and hydrogen at the anode and cathode, respectively [3].

In electrochemical ozone generation, this process is modified by using an anode material such as Nickel and antimony doped tin oxide (NATO), PbO_2, and Boron doped diamond (BDD) that can catalyze the conversion of oxygen into ozone. Christensen and co-workers [5] reported a current efficiency of 50% in sulphuric acid; this extremely high selectivity. An electrode normally made of a metal such as platinum or titanium, which can facilitate the transfer of electrons from the oxygen molecules to create ozone [1-4]. NATO is a composite material that is effective to generate ozone due to its properties such as a high surface area and good electrical conductivity which

allows for efficient active site reactions and facilitates the transfer of electrons [3].

One of the main advantages of using NATO electrodes for electrochemical ozone generation is that they are relatively inexpensive and easy to produce. Additionally, NATO have a high catalytic activity for ozone generation. However, the current efficiency of ozone could not have predicted. Therefore, this research focused on the effect of nickel concentration on antimony doped tin oxide which examined electrocatalytics activity and the surface properties for ozone generation.

2. Methodology

2.1 Synthesis method and electrode preparation

The preparation of anodes and Sol-gel method to fabricate Nickel-Antimony doped Tin Oxide anodes (NATO) were adapted from Maneelok, S. and Attidekou, P. [1]. The precursor solutions contained $SnCl_4.5H_2O$, $SbCl_3$ and $NiCl_2.6H_2O$, in the mole ratio Sn:Sb:Ni of 98:1.5: x, where x was 0.5-3. All chemicals were dissolved in ethanol. The 0.8*0.8 cm foil substrates were dipped in the catalyst solutions and were then calcined in a furnace at 450 °C for 1 hour. The electrodes were weighed after allowed to cool in air.

2.2 Analytical method

The anodes were characterized for structure, morphology and chemical composition. The examination of structure was carried out by the X-ray diffraction (XRD). Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) were employed to observe the morphology and chemical composition, respectively. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical state of catalyst. The generation of ozone was measured by Electrochemical oxidation process. 0.5M H_2SO_4 was employed as electrolyte. A Pt-Ti mesh was employed as a cathode. Both electrodes were comprised the cuvette cell and placed in the cuvette holder in an UV spectrophotometer. A reference spectrum was collected with the potential at 2.7V for 30s. The steady state absorbance at 258 nm was used to calculate the ozone current efficiency, assuming an extinction coefficient of 3000 $M^{-1}cm^{-1}$ [5].

The current efficiency of ozone (%CE) can be calculated as shown in Eq.(1):

$$\eta = 58.A_{O3} / Q \quad (1)$$

Where A is the ozone absorbance and Q is the charge passed.

The current was collected from power supply with the potential at 2.7V for 30s, then it was divided by anode area to calculate for current density.

3. Results and Discussion

3.1 The anodes characterisation

Nickel and antimony doped tin oxide (NATO) were prepared by sol-gel method with various Ni doping level (0.5-3%Ni) and calcined at 450 °C. The XRD patterns of all NATO materials in Fig. 1 showed a single phase of rutile structure (Cassiterite, syn; Q: S; 00-041-1445) which was obtained from the ICDD crystallographic data base. The peak position of the XRD patterns were ascribed to (110), (101), (020), (121), (220), (002), (310) and (112) planes of SnO_2 which is correspondent to with crystallographic data base [1]. No secondary phase and impurities were observed. This suggests that the Sb and Ni ions substitute for the Sn ions in the crystal lattice of bulk SnO_2, in agreement with the literature [4][6].

From Fig.1, it can be seen that the diffraction peaks of NATO materials with Ni content from 0.5% to 3% were relatively the same the position peaks of those, resulting no effect of Ni content with the maximum of 3%Ni on the structure. This results corresponded to the work of Christensen et.al [4] and Sun et.al. [6]. The authors reported the XRD pattern of NATO with Ni dopant up to 5% mole that the diffraction peaks were presented the same position and no secondary phase was observed. This can indicate that the ion radius of Sb^{5+} and Ni^{2+} smaller than Sn^{4+} therefore they might be replaced Sn^{4+} ions in the lattice [4][6].

Fig.2 showed the SEM image and EDX spectra of 1.5NATO anode with magnification of 60000x. It can be seen that the NATO anode morphology presented the spherical shape and well dispersed in nanocatalyst. Regarding effect of Ni content, it was found that the shape of NATO materials did not change, indicating no effect from Ni dopant concentration up to 3%. Moreover, the spherical shape could provide more surface area for catalytic activity to produce ozone. EDX spectra in Fig. 2 reveals that Sn, Sb and O were detected, however there still have nickel in NATO because a tiny amount of nickel was added in antimony doped tin oxide and nickel ion are also substitute in the bulk of lattice of SnO_2. EDX techniques examined the surface of NATO, so this might be due to undetected Ni peak.

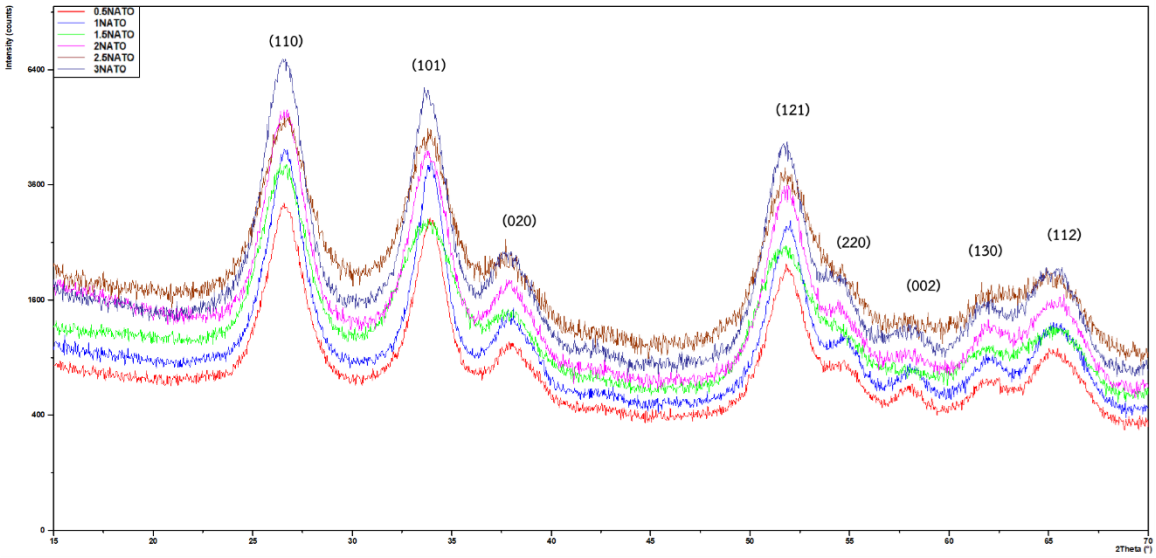

Fig.1. XRD pattern of NATO materials with varying Ni content from 0.5%Ni to 3%Ni and calcined at 450°C

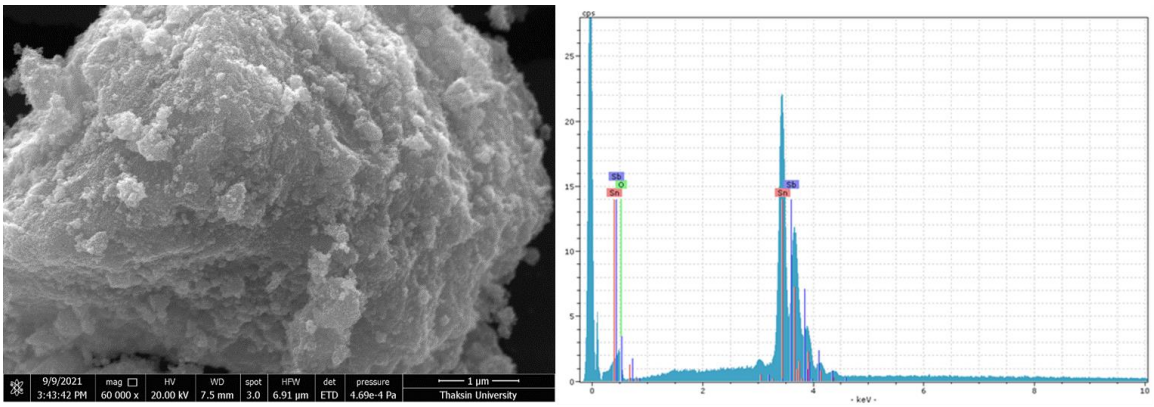

Fig.2 A typical SEM image and EDX spectra of 1.5NATO anode

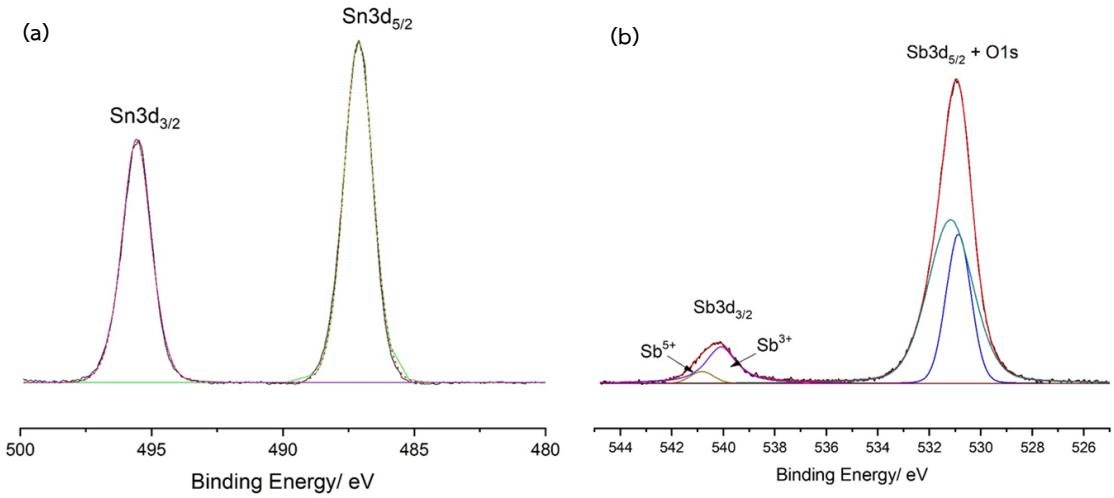

Fig.3 XPS spectra of 1.5NATO sample calcined at 450°C: (a) the fitted XPS spectra of Sn 3d state and (b) the fitted XPS spectra of Sb 3d state.

The XPS technique was employed to analyse chemical oxidation state as shown in Figure.3. Fig. 3(a) shows the Sn 3d peak splits into Sn 3d3/2 and Sn 3d5/2. Both peaks were fitted at binding energy (BE) of 495.57 and 487.19 eV, respectively. Accordind to chemical oxidation state, the BE was assigned the state of Sn^{4+} in the form of Ni/Sb-SnO_2 [1][7]. It can be seen in Fig.3(b) show an asymmetric two peaks which was splited to Sb 3d5/2 and Sb 3d3/2. The Sb 3d5/2 peak are broad asymmetric and overlaps with O1s peak, suggesting contributions from other oxygen species such as lattice oxygen species (MOx), bonded oxygen metals (M-O) and metal hydroxides (M-OH). Li et. al.[8] reported that the BE around 532.11 eV attributed to adsorbed oxygen (Oads) that lead to oxygen evolution potential (OEP). It indicated that plays an important role in electrochemical oxidation with O_2 and O_3. Furthermore, the Sb 3d3/2 peak is generally employed to determine the oxidation state of Sb. The BE of Sb 3d3/2 was observed at 540.61 eV and 541.49 eV corresponding to Sb^{3+} and Sb^{5+}, respectively. The study correspond to other researches [1][4][6][8].

3.2 Electrochemical Ozone Generation

With respect to ozone production as a function of Ni content in Fig. 4, the current efficiencies were in the range of 15% - 19% for Ni content between 0.5% and 3%. The results in Fig.4 shows that the optimal of nickle content at 1.5%Ni presented a maximum of ozone genration ca. 19%. This obtained results is not good compared with Maneelok et.al [1]. They investigated ozone current efficiency of 2NATO calcined at 700 °C and found that highest current efficiency of ca. 37% and current density at 0.22 A cm^{-2}. This might be due to affect of calcination temperature. Regarding effect of Ni content, the current efficiency decreased as a function of Ni doping level and it showed the same behaviour when increasing the electrolysis time. This might be due to increase resistant in order to Ni doping level. It was reported that the resistivity of NATO rosed with function of Ni level [9]. With respect to electrolysis time, as seen from Fig.4, the current efficiency decreased as a function of time. It can elucidated that ozone decay to •OH radicals when increasing electrolysis time.

With respect to current density in Fig.5, the results show that the current density decreased with increasing Ni content due to decrease the electrocatalytic [1]. The current density were in the range of 0.06 A cm^{-2} - 0.08 A cm^{-2} for Ni content between 0.5%Ni and 3%Ni at 2.7V for 30s. From the literature, the maximum current densities reported by Christensen et al. [5] are 100 mA cm^{-2} with the cell voltage > 2.7 V in 1M $HClO_4$.

The results have a good agreement with the work reported by Parsa and co-workers [10] who observed the electrochemical ozone generation on the 2.5 cm x 2.5 cm NATO anode at 2.4 V for 600s. The author found that the current density and current efficiency decreased with increasing the time. This may be due to side reactions between OER and EOP, and O_2 evolution of •OH radicals [1][6], for example, reaction in Eq.2

OH: $OH\bullet + O_3 \longrightarrow O_2 + HO\bullet_2$ (2)

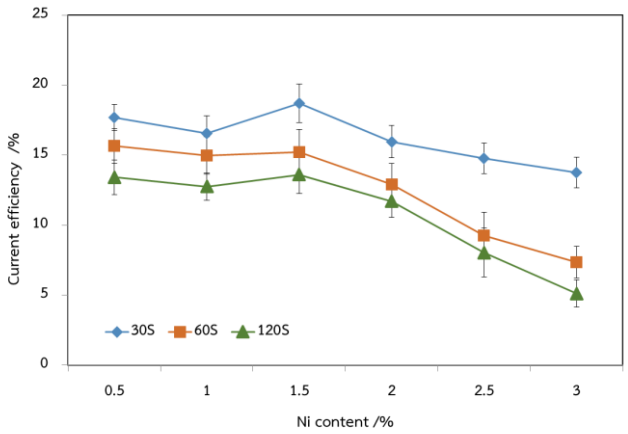

Fig.4 Plot of current efficiency of NATO anodes as a function of Ni concentration in 0.5M H_2SO_4 at 2.7V for electrolysis time between 30 s and 120 s.

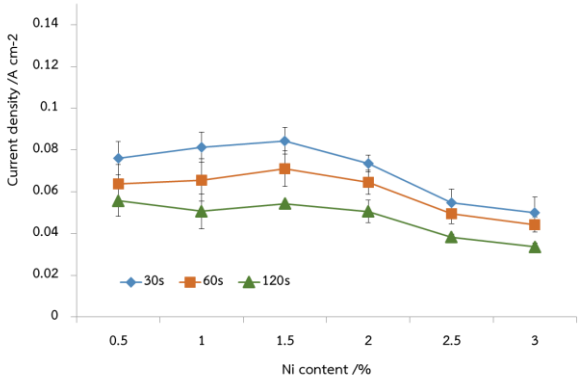

Fig.5 Plot of current density of NATO anodes as a function of Ni concentration in 0.5M H_2SO_4 at 2.7V for electrolysis time between 30s and 120s.

4. Conclusions

The Nickel and antimony doped tin oxide anodes with various of Ni content between 0.5% and 3% calcined at 450 °C prepared by dip-coating method. All NATO show a single phase rutile structure with Sb^{5+} and Ni^{2+} ions replacing into Sn^{4+} ions in the SnO_2 lattice due to the ion radius. The anode morphology shows spherical shape and well dispersed. With respect to the chemical oxidation state of NATO, the binding energy of the Sb 3d3/2 was at 540.61 eV and 541.49 eV agree with Sb^{3+} and Sb^{5+}, respectively. In addition, the ozone activity of NATO anodes as a function of Ni content presents the maximum current efficiency of 18.7% with the current density ca. 0.08 A cm^{-2} in 0.5 M H_2SO_4 at 2.7V. The optimal Ni content was 1%Ni. Furthermore, the current efficiency and current density decrease with increasing electrolysis time as a result of produce more •OH radicals, causing decay the ozone activity.

Acknowledgement

This work was supported by National Higher Education, Science, Research and Innovation Policy Council, Thaksin University (Research project grant) Fiscal Year 2022.

References

[1] Maneelok, S. and Attidekou, P. (2022). Effect of Nickel Concentration on Ozone Production using Nickel-Antimony Doped Tin Oxide for Wastewater Treatment. *ASEAN J. Sci. Tech. Report*, 25(2), 50-58.

[2] Supandee Maneelok, Pierrot S. Attidekou., Paul A. Christensen. (2018). In Application of electrochemical ozone generation on Nickel/antimony-doped tin oxide (Ni/Sb-SnO_2) electrodes to decolourisation and degradation of Reactive Blue 50 dye, Challenging in Environmental Science and Engineering (CESE2018), Bangkok, Thailand, 7-8 November 2018.

[3] Christensen, P. A., Yonar, T., Zakaria, K. (2013). The Electrochemical Generation of Ozone: A Review. *Ozone-Science & Engineering*., 35 (3): 149-167.

[4] Christensen, P. A., Attidekou, P. S., Egdell, R. G., Maneelok, S., Manning, D. A. C., & Palgrave, R. (2017). Identification of the Mechanism of Electrocatalytic Ozone Generation on Ni/Sb-SnO_2. *The Journal of Physical Chemistry C*, 121(2), 1188-1199.

[5] Christensen, P.A., W.F. Lin, H. Christensen, A. Imkum, J.M. Jin, G. Li, and C.M. Dyson. (2009). Room Temperature, Electrochemical Generation of Ozone with 50% Current Efficiency in 0.5M Sulfuric Acid at Cell Voltages < 3V. *Ozone: Science & Engineering*, 31(4): p. 287-293

[6] Sun Z.R.; Zhang, H.; Wei, X.F.; Ma, X.Y., Hu, X. (2015) Preparation and electrochemical properties of SnO2-Sb-Ni-Ce oxide anode for phenol oxidation. *Journal of Solid State Electrochemistry*, 19(8): p. 2445-2456.

[7] Yang, S. Y., Choo, Y. S., Kim, S., Lim, S. K., Lee, J., Park, H. (2012). Boosting the electrocatalytic activities of SnO_2 electrodes for remediation of aqueous pollutants by doping with various metals. *Applied Catalysis B-Environmental*., 111 : 317-325.

[8] Li, X., Shao, C., Yu, J., Zhu, K. J. I. J. E. S.(2019). Preparation and investigation of nickel-antimony co-doped tin oxide anodes for electro-catalytic oxidation of organic pollutions., 14 : 205-218.

[9] Wang Y.H.; Chan, K.Y.; Li, X.Y.; So, S.K. (2006). Electrochemical degradation of 4-chlorophenol at nickel–antimony doped tin oxide electrode. *Chemosphere*, 65(7), pp. 1087-1093.

[10] Parsa, J.B., M. Abbasi, and A. Cornell, (2012). Improvement of the Current Efficiency of the Ti/Sn-Sb-Ni Oxide Electrode via Carbon Nanotubes for Ozone Generation. *Journal of The Electrochemical Society*, 159(5): p. D265-D269.