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Electrolytic Generation of Ozone on Antimony- and Nickel-Doped Tin Oxide Electrode

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In a recent report, ozone was produced with high efficiency in perchloric acid on an anode coated with antimony-doped tin oxide. We report here that high current efficiency can be enhanced if trace amounts of a second dopant, nickel, is present. The effect of composition of the coating in terms of Ni:Sb:Sn was carefully analyzed. The optimum Ni:Sb:Sn ratio, determined to be 1:8:500, was determined giving a corresponding ozone generation current efficiency of over 30% at room temperature. The highest current efficiency was observed at an optimum operating potential of 2.2 V vs Ag/AgCl. Electrolytic generation of ozone in perchloric acid, sulfuric acid, and phosphoric acid at different concentrations was also studied and compared. In 0.1 M H₂SO₄, the ozone concentration reached 34 mg/L and a current efficiency of 36.3% could be achieved. This is about the highest current efficiency ever reported for electrolytic generation of ozone in an aqueous medium at room temperature.

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There is an increased usage of ozone for disinfection, environmental cleanup, and chemical syntheses. Ozone is commonly generated in air by corona discharge at a very high voltage. The use of small piezo electric elements has made miniature ozone generators popular in various consumer and household applications. The high-voltage generation of ozone in air will lead to small amounts of undesirable side products of nitrogen oxides.¹ The generation of ozone in aqueous media by direct electrolysis is therefore a very attractive alternative, particularly if dissolved ozone is needed. The much lower voltage in electrolysis eliminates any possibility of nitrogen oxide generation and promises higher energy efficiency. Any losses of current efficiency will mostly lead to the production of oxygen, which in many cases can be useful. Dissolved ozone generated through water electrolysis has been studied since the early eighties. Several anode materials have been explored, including Pt, PbO₂, diamond, and glassy carbon, but only Pt and PbO₂ showed appreciable current efficiency for ozone generation.²⁻¹² Platinum anode showed a high current efficiency of 35% at about -50°C.⁶ At room temperature, however, the current efficiency fell to 0.5%.⁶ As an anode material, PbO₂ can generate ozone with current efficiency of about 13% at room temperature.⁴ Lead materials and alloys, however, are very undesirable for the potential health hazards they bring. Recently, the European Union issued a directive on the restriction of the use of lead and alloys in electric and electronic equipment.

Tin dioxide is a semiconducting material with high oxygen evolution overpotential. This material has been studied for gas sensing and direct electrochemical degradation of dissolved organics in water.¹³⁻¹⁵ The study of undoped tin dioxide as anode material for electrolytic generation of ozone was reported in concentrated sulfuric acid with a low current efficiency and low stability.⁴ In a recent report, Cheng and Chan¹⁶ investigated antimony doping of tin dioxide as a novel anodic material for ozone electrolytic generation. They reported high current efficiency and high dissolved ozone concentration at room temperature. It was found recently that the performance of the antimony-doped tin dioxide can be strongly affected by the presence of trace amount of a second dopant. In this paper, we report a detailed study of the effect of adding nickel to antimony-doped tin dioxide on ozone generation. In addition to the composition of the anode coating, effects of the concentration, and type of acid, parameters in anode preparation were also studied.

Experimental

The anode was prepared by coating a titanium substrate with an alcohol solution containing tin, antimony, and nickel precursors, followed by pyrolysis at 500°C. The preparation procedure was the

same as previously described¹⁶ except for the addition of a nickel precursor. The substrate was a 0.5 mm titanium foil supplied by Good Fellow Inc., U.K. Chloride precursors were used and obtained from different suppliers as follows: SbCl₃ (BDH, 99.5%), SnCl₄ · 5H₂O (98%, ABCR), and NiCl₂ · 6H₂O (Merck, 98%). The precursors with a definite Ni:Sb:Sn ratio were dissolved in absolute ethanol (APS, 99.5%). A 0.8 × 0.8 cm titanium foil (99.95% Good Fellow) was treated in boiling 10% oxalic acid for 1 h, washed with distilled water, and dried. The dip coating and pyrolysis procedure was repeated seven times, except where otherwise mentioned. In the final heating step, the electrode was heated for a longer duration of 1 h. The scanning electron micrograph (SEM) of a typical electrode prepared is shown in Fig. 1. The electrode surface was covered with connected uniform nanoparticles 5–10 nm in diameter.

Electrolysis to generate ozone was performed in a standard quartz cell designed for UV spectrophotometer, as illustrated in Fig. 2. The UV cell top cover had three holes for the reference electrode, the anode working electrode, and the counter electrode (cathode) to be electrically connected to the potentiostat. A silver wire coated with silver chloride was used as the reference electrode. The counter electrode was a small platinum foil placed in the top region of the UV cell to avoid any disturbances to the working electrode placed flat at the bottom of the cell. The reference electrode and cathode were placed against the cell wall. The configuration of the three electrodes had no interference with the optical path of the UV light. The cell was filled with 3 mL of electrolyte. The electrolysis potential was controlled by a Radiometer Copenhagen/Dynamic-Eis Voltalab PGZ301 potentiostat/galvanostat. The three types of acids used for electrolysis were perchloric acid (AJAX Chemicals), sulfuric acid (Merck), and phosphoric acid (Mallinckrodt).

The concentration of dissolved ozone was determined in situ by an UV spectrophotometer (Perkin Elmer, Lambda 20). The UV spectrum was calibrated by the standard indigo method.¹⁷ For the UV spectrophotometer used, 1 mg/L dissolved ozone gave an absorbance of 0.098 at the wavelength of 258 nm. The UV spectra for several concentrations of ozone are shown in Fig. 3. In addition to in situ determination by UV spectroscopy, the solution was sampled in a few runs to determine the ozone concentration by the indigo titration method. The ozone concentrations determined by the two methods were in agreement as also reported previously in the literature.¹⁷ The in situ UV determination was therefore accurate and consistent. The current efficiency was determined by counting the coulombs passed and comparing it to the theoretical value required to generate the measured amount of ozone, according to Faraday's law with the overall reaction of

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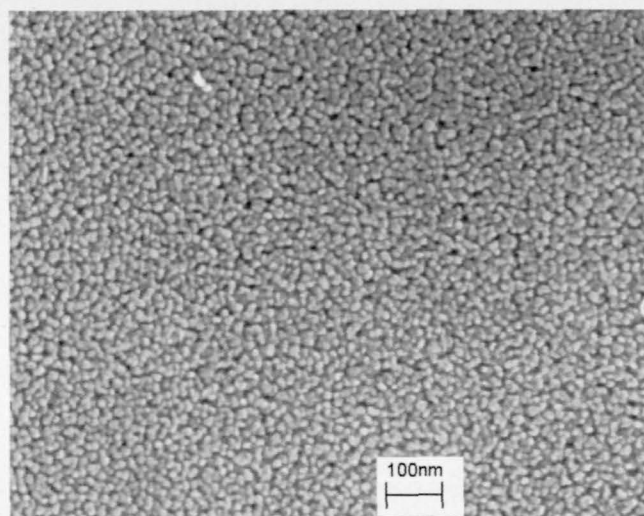
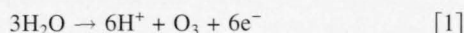


Figure 1. The scanning electron micrograph of a typical electrode prepared by wet coating followed by pyrolysis at 500°C.



Ozone was likely not to be generated by this six-electron reaction step but instead by two or more steps involving the generation of intermediates such as dioxygen. If all the dioxygen generated were consumed to generate ozone, then the efficiency would be the same, because a total of six electrons was transferred in the overall reaction. To have a consistent comparison, we calculate the current efficiency in the first 2 min of constant potential electrolysis experiment. Typical dissolved ozone concentration could reach up to 34 mg/L. Typical steady-state current density was about 15 mA/cm². We recognized that, in almost all electrolysis experiments, there was high enough ozone generated in the aqueous phase that a certain amount of ozone escaped into the gas phase and was not detected by the UV analysis. The UV beam was directed only through the liquid phase. All reported current efficiencies were based on dissolved ozone. Higher current efficiencies would have been reported if gaseous ozone concentration and gas volume were also determined.

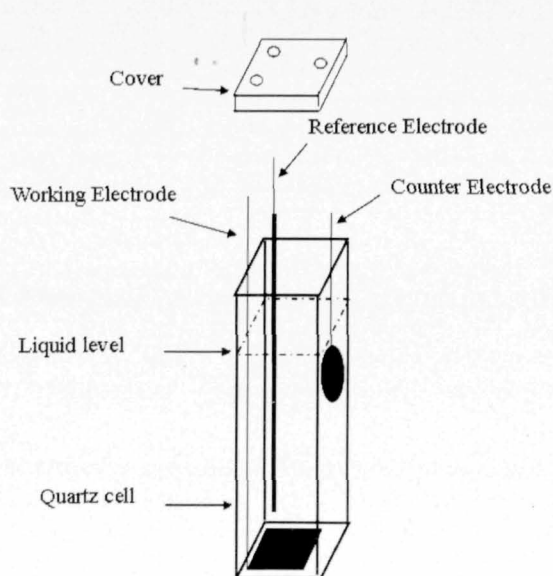


Figure 2. A schematic drawing of the electrolysis UV cell showing the arrangement of the working electrode, reference electrode, and the counter electrode.

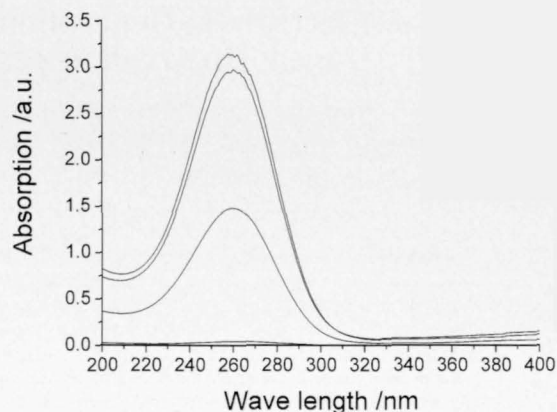


Figure 3. UV spectra of sample solutions with dissolved ozone concentrations at 0.42, 14.7, 29.8, and 31.4 mg/L (four curves from bottom to top).

Results and Discussion

Electrochemical characterization of anode.— Typical cyclic voltammograms (CVs) of the anode with or without nickel dopant are shown in Fig. 4. The Sb–Ni-doped SnO₂ anode was prepared by coating with a precursor solution containing the three elements in atomic ratio of Sn:Sb:Ni = 1000:16:2. For the SnO₂ electrode doped only with antimony but no nickel, the atomic ratio of the Sn:Sb was 1000:16. The cyclic voltammetry was performed at 50 mV/s in 0.1 M HClO₄ at room temperature. From Fig. 4, the onset potential was about 1.7 V vs Ag/AgCl, which is much higher than the typical value expected for oxygen evolution in acid solution, indicating that oxygen evolution was kinetically suppressed. Though the two Sb-doped SnO₂ electrodes with or without nickel doping showed similar onset potential, the one with nickel had a faster rise in current. Within the scanned voltage range, CVs of both electrodes did not have any peaks or shoulders. There was no cathodic current on the reverse scan and consecutive CV scans were reproducible. These suggest a stable electrode surface without the oxidation or reduction of transient or surface species. The SEM micrograph of the electrode after the electrolysis had no observable morphology changes compared to that of a fresh electrode shown in Fig. 1. As shown in the CV characterization, the anodic current above 1.7 V (Ag/AgCl) correlates to the detection of dissolved ozone. In addition, there was the detection of the characteristic smell of ozone in the gas phase.

The effect of composition of the anode coating.— Before we investigated the effect of nickel and the optimal composition of Sn:Sb:Ni for maximum ozone generation, we determined the best applied

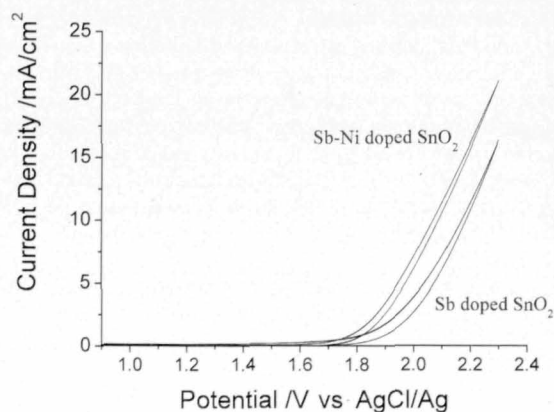


Figure 4. Cyclic voltammograms of Sb-doped and Sb–Ni-doped SnO₂ electrodes in 0.1 M HClO₄ at room temperature and at a scan rate of 50 mV/s.

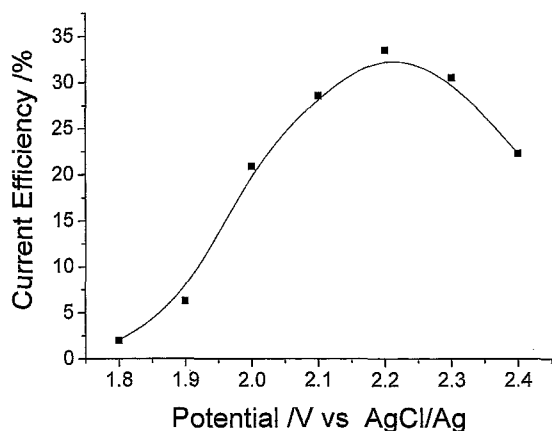


Figure 5. The effect of applied potential on current efficiency of ozone generation in 0.1 M HClO₄ at room temperature.

potential for the highest ozone generation. For these experiments to optimize applied potential, the anode was prepared from the precursor solution containing Sn, Sb, Ni in concentrations of 1000, 16, and 2 mM, respectively. Electrodes were freshly prepared and seven coating cycles were performed with pyrolysis carried out at 500°C. The electrolysis was performed at constant potential in 0.1 M HClO₄. The effect of applied potential on ozone generation current efficiency is shown in Fig. 5. The results showed an optimal potential of 2.2 V vs Ag/AgCl with the highest current efficiency of 32.5%. From Fig. 4, the anodic branch beyond 2.2 V (Ag/AgCl) of the CV shows a linear rise with increasing potential. The current efficiency in Fig. 5 also rises monotonically but decreases after 2.2 V. This decline of current efficiency suggests either an increase of the competing side reaction of oxygen evolution or an increase in ohmic losses due to lower conductivity in the solution when gas bubbles are generated.

To investigate the effect of anode composition, it would be desirable to have an elemental characterization of the solid surface of the anode used in the electrolysis experiments. Our main objectives were to determine the optimal amount of antimony and nickel, relative to that of tin. We attempted energy dispersive X-ray analyses (EDX), but unfortunately the location of antimony peaks overlapped with that of tin and the amount of nickel (<1% relative to Sn) was too small to be detectable by EDX. Here, we correlate ozone generation to metal compositions of the precursor solution. Because the precursor solution has a direct effect on the final composition of the anode surface, and the recipe of preparing the material is important to the ultimate application, we believe this will be an effective approach to investigate the effect of composition. In our previous study,¹⁶ there was a significant deviation in the Sn:Sb ratio of the precursor solution (100:1) and the ultimate anode surface analyzed by inductively coupled plasma (ICP) (7:1). It is expected that higher relative Sb concentration may be present in the solid surface after repeated coating and pyrolysis. To prepare different compositions of anodes, the SnCl₄·5H₂O in the ethanol solution was kept at 1 M, whereas the relative ratios of the three metals changed by varying the concentration of NiCl₂·6H₂O and SbCl₃ in the solution. The electrodes were all prepared by seven coating cycles with pyrolysis at 500°C. The electrolysis of the anodes in 0.1 M HClO₄ was performed at room temperature at a constant potential of 2.2 V vs Ag/AgCl. Figure 6 plots the ozone current efficiency as a function of Sb:Sn ratio. For each plot, the Sb:Ni ratio was fixed and the effect of Ni addition may be seen by comparing among the family of curves of fixed Sb:Ni ratio. An optimum Sb:Ni ratio (8:1) and Sn:Sb ratio (1000:16) are clearly identified within the matrices of experiments performed. The combined optimum Sn:Sb:Ni composition in the coating solution is therefore 1000:16:2 (mM), respectively. The maximum current efficiency in the electrolysis was about 32.5%. To

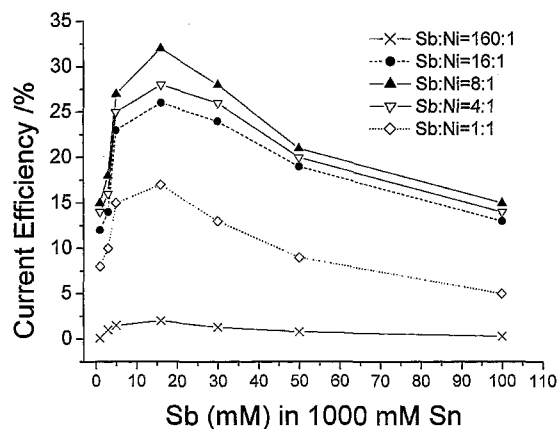


Figure 6. The effect of coating solution compositions on current efficiency of ozone generation in 0.1 M HClO₄ at room temperature at an applied potential of 2.2 V (Ag/AgCl).

our best knowledge, this is the highest current efficiency reported for electrolytic generation of ozone at room temperature in any aqueous medium.

The optimum Sn:Sb ratio of 1000:16 in the precursor solution roughly agrees with the value of 1000:10 in our previous study.¹⁶ As shown in Fig. 6, nickel, though present in trace amounts, has a critical effect on ozone generation. Without nickel dopant, the current efficiency is very low. In our previous communication, which focused only on Sb-doped SnO₂, nickel was neither added nor investigated, but was probably present as a contaminant and led to the rather high ozone generation reported. It is suspected that the addition of nickel may have an effect on (i) the oxidation state of Sb and/or Sn; (ii) the electronic binding energy and bandgap of the doped semiconducting material; (iii) the electronic or ionic conductivity of the material; and (iv) the oxygen affinity of the solid surface. With more solid surface characterizations in the future, we will investigate these factors on ozone generation and perhaps help to elucidate the reaction mechanism. While a single antimony dopant to tin oxide was not very effective, we have investigated a number of other second metal dopants, in addition to nickel. These included cobalt, iron, rhodium, copper, and ruthenium. No enhancing effect on ozone generation was observed for the additions of these metals to the coating solution.

Amount of electrode coating.— We should consider whether the underlying Ti substrate was sufficiently covered or not, especially when only one or two coatings were performed. Titanium has a high oxygen evolution overpotential >1.8 V (vs Ag/AgCl). No ozone

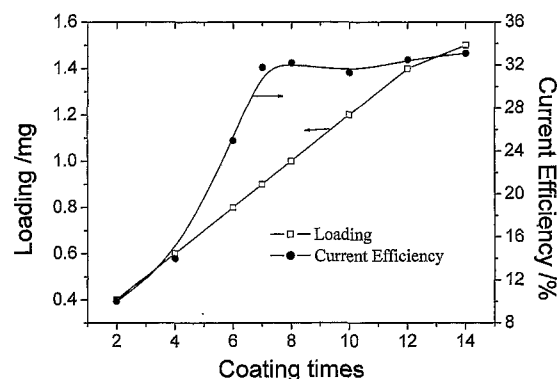


Figure 7. The effect of amount of coating on current efficiency of ozone generation in 0.1 M HClO₄ at room temperature at an applied potential of 2.2 V (Ag/AgCl).

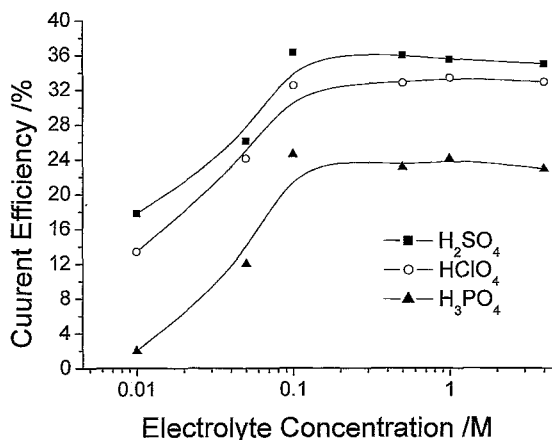


Figure 8. The effect of electrolyte on the current efficiency of ozone generation at room temperature at an applied potential of 2.2 V (Ag/AgCl).

generation can be detected from a titanium anode, even at higher potentials. At the potential at which electrolysis experiments were conducted (2.2 V vs Ag/AgCl), an exposed titanium substrate may have a large effect on efficiency, because more oxygen may be generated on titanium. At the same time, ozone generation depends on the amount of the active materials coated. We investigated this effect of coverage of titanium substrate and the amount of active coating materials by comparing the performance of electrodes with a different number of coatings. A fixed amount of the precursor solution composed of Sn:Sb:Ni = 1000:16:2 was deposited in each coating step, followed by pyrolysis at 500°C. The amount of active material is proportional to the number of coating steps performed, as shown in Fig. 7. Loading in each coating step was determined as the difference of the mass of the coated electrode after pyrolysis and the mass of the electrode before wet solution was applied. Ozone current efficiencies were determined by the electrolysis in 0.1 M HClO₄ under a constant potential of 2.2 V vs Ag/AgCl. From Fig. 7, current efficiency increases steadily with loading of active material until seven coatings, after which additional coatings have little effect on ozone generation. This indicates that, with seven coatings, either the titanium substrate was fully covered or the utilization of the doped SnO₂ material has reached a maximum. The thickness of the coating calculated from the weight gain was about 1.0 μm for seven coatings, assuming the coating density to be that of SnO₂ (6.9 g cm⁻³). If a significant thickness of the coating contributes to ozone generation, mass transfer and ohmic resistance are also factors limiting further increase of current efficiency.

The effect of acid electrolytes.—Ozone generation efficiency was found to differ in different acidic media⁴ and at different concentrations. The concentration of acid will directly affect proton concentration. The type of acid anions also has a significant effect, probably due to selective adsorption on electrodes. We investigated the effect of acid type and acid concentration on ozone generation current efficiency. The same electrode preparation and electrolysis conditions were used, as in the earlier discussion. Three common acids, perchloric, sulfuric, and phosphoric, were used, representing anions of different valence charges. In Fig. 8, the effect of acid

concentration is similar for the three acids. A linear rise region in current efficiency was seen until about 0.1 M, after which a steady maximum current efficiency was observed. The type of anion has a large effect on ozone generation. The highest efficiency was achieved in H₂SO₄, while a slightly lower current efficiency was found in HClO₄. No correlation can be made with the valences of the anions, and phosphoric acid is likely to be present in different ionization forms. It is also known that SO₄²⁻ has stronger adsorption compared to ClO₄⁻, particularly at higher potentials. The effect of acid anion may be related to intermediate steps of the reaction mechanism, and further investigations are warranted.

The reported findings show a very promising material for ozone generation in aqueous media, with many advantages over the conventional technology. Parameters of the coating composition and preparation procedure have been optimized. Further experiments are needed to correlate material properties to performance and to reveal steps of the reaction mechanism.

Conclusions

Nickel- and antimony-doped tin dioxide electrode showed a remarkably high current efficiency of over 30% for electrolytic ozone generation at room temperature. The optimum parameters for maximum ozone generation have been identified, including (i) composition of the dopants in the precursor solution; (ii) applied potential of electrolysis; (iii) effective amount of coating material; and (iv) concentration and type of acid anion. The optimum precursor solution contains 1000 mM tin, 16 mM antimony, and 2 mM nickel. Sulfuric acid gives the highest current efficiency, at or above 0.1 M acid concentration.

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