

Comparison of Ti/BDD and Ti/SnO₂–Sb₂O₅ electrodes for pollutant oxidation

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Abstract

Anodic oxidation is a promising process for degrading toxic and biologically refractory organic pollutants present in wastewater treatment. Proper selection of electrodes is the key to reach effective and economic operation. In this study, two types of electrodes, i.e. the recently developed Ti/BDD and Ti/SnO₂–Sb₂O₅, which is generally believed to be superior to the conventional electrodes, were compared under the same conditions. It was found that the Ti/BDD electrode could mineralize both phenol and reactive dyes effectively. But the Ti/SnO₂–Sb₂O₅ electrode could only mineralize phenol. When oxidizing more refractory reactive dyes, it demonstrated very poor activity. In addition, the Ti/BDD electrode had a service life of 264 h in an accelerated life test, but the Ti/SnO₂–Sb₂O₅ was irreversibly damaged within several seconds. The direct experimental comparison in the present study indicates that the Ti/BDD electrode is much better than the Ti/SnO₂–Sb₂O₅ electrode for pollutant oxidation.

1. Introduction

In the past two decades, anodic oxidation has been widely investigated for wastewater treatment. Its high oxidation efficiency, fast reaction rate, and easy operation make it a very attractive alternative to the conventional processes for degrading toxic and biologically refractory organic pollutants. It is well known that proper selection of electrodes is of great importance for effective and economical operation. Good electrodes should be not only effective for pollutant degradation, but also stable electrochemically. Up to date, numerous types of electrodes including Pt [1], graphite [2, 3], PbO₂ [4–8], SnO₂ [7, 9–11], IrO₂ [11–13], Pt–Ir [14], RuO₂ [15], glassy carbon [16], fiber carbon [17], MnO₂ [18, 19], TiO₂ [20, 21], and boron-doped diamond (BDD) have been investigated. SnO₂ electrodes are generally believed to be superior to Pt, graphite, PbO₂, and many other common electrodes. Pure SnO₂ is an n-type semiconductor with a band gap of about 3.5 eV. This kind of oxide exhibits very high resistivity at room temperature and thus cannot be used as an electrode material directly. However, its conductivity can be improved significantly by doping Ar, B, Bi, F, P or Sb [9, 22–27]. Doped SnO₂ films are usually used as transparent electrodes in high-efficiency solar cells, gas detectors, far IR detectors and transparent heating elements [28]. Kotz and co-workers [9] first reported anodic oxidation of organic compounds on the Sb-doped SnO₂ electrode

using Ti as a substrate (Ti/SnO₂–Sb₂O₅). The current efficiency obtained on the Ti/SnO₂–Sb₂O₅ electrode was about 5 times higher than that on Pt [10]. Comninellis [11] investigated anodic oxidation of phenol on different electrodes. It was found that Ti/SnO₂–Sb₂O₅ showed higher capability of completely oxidizing phenol than PbO₂, IrO₂, RuO₂ and Pt. The current efficiency obtained for a degradation degree of 71% in oxidizing 10 mM phenol on Ti/SnO₂–Sb₂O₅ under a current density of 500 A m⁻² at 70 °C was 58%, over three times higher than on the other electrodes. Grimm and coworkers [29] investigated phenol oxidation on Ti/SnO₂–Sb₂O₅ and PbO₂ using a cyclic voltammetric method and also found that the former was more active.

In recent years, a new type of electrode material, i.e. BDD, has received growing attention for pollutant oxidation. Undoped synthetic diamond is an insulator with a resistivity of > 10⁶ Ωm and a band gap energy of 5.5 eV [30]. However, the conductivity of diamond can be significantly improved by doping with boron. Usage of BDD electrodes for pollutant removal was first reported by Tenne and co-workers in 1993 [31]. They investigated the reduction of nitrate to ammonia on a BDD cathode. Carey and coworkers [32] patented the use of BDD electrodes as anodes for organic pollutant oxidation in 1995. Since then, anodic oxidation of various model pollutants such as phenol [33, 34], cyanide [35], carboxylic acids [36], 3-methylpyridine [37], 2-naphthol [38], 4-chlorophenol [39], 4-chlorophen-

oxyacetic [40, 41], benzoic acid [42], polyacrylates [43], and dyes [44] on BDD electrodes was investigated. The current efficiency ranged from 33.4% to 95%, depending on pollutant properties and operational conditions.

BDD films are usually synthesized on Si substrates from a gaseous mixture of H_2 and CH_4 using chemical vapor deposition (CVD). Since Si is poor in mechanical strength and low in electrical conductivity, Si/BDD electrodes can be employed only at laboratory scale. In our previous studies [45, 46], BDD films with well-defined diamond features have been successfully deposited on Ti substrates by optimizing the CVD conditions and improving the gas composition. This increases the feasibility of industrial application of synthetic BDD thin film electrodes to wastewater treatment. Preliminary experimental results have showed that the Ti/BDD electrode is preferable to the Ti/SnO₂-Sb₂O₅ electrode, but more extensive investigation is needed.

The objective of the present study is to give an overall comparison of the Ti/BDD and Ti/SnO₂-Sb₂O₅ electrodes. The cyclic voltammetric behavior was investigated first to reveal the basic electrochemical performance difference. Then, phenol and 15 reactive dyes were used as model pollutants to compare the activity of the Ti/BDD and Ti/SnO₂-Sb₂O₅ electrodes under the same conditions. Finally, accelerated life tests were conducted to compare the electrochemical stability. The results obtained will help to select appropriate electrodes for anodic oxidation of pollutants.

2. Experimental section

2.1. Chemicals

All chemicals, including B(CH₃O)₃ (99.999+%, Aldrich, WI), CH₂(OCH₃)₂ (99.5+%, Acros, NJ), SnCl₄ · 5H₂O (98+%, Acros, NJ), SbCl₃ (99+%, Acros, NJ), Na₂SO₄ (99+%, Aldrich, WI), iso-propanol (99.7%, Lab-scan, Bangkok, Thailand), hydrochloric acid (37%, Riedel-deHaen, German), and concentrated sulfuric acid (Acros, NJ), phenol (ultra-pure, GibcoBRL, NY), and dyes were used as received.

2.2. Electrode preparation

BDD films were synthesized from a gaseous mixture of H_2 , CH_4 and $CH_2(OCH_3)_2$ with hot filament chemical vapor deposition (HFCVD). B(OCH₃)₃ was used as a boron dopant. Ti disks, 2 mm thick and 12.7 mm in diameter, were used as substrates. Before deposition, the substrates were sandblasted, then scratched with diamond paste (1 μm, Kemet International Ltd, UK), cleaned ultrasonically with acetone and, finally rinsed with deionized water. It was found that the quality of Ti/BDD electrodes depended strongly on the HFCVD conditions. The appropriate parameters are: 0.8% CH_4 in H_2 , carbon ratio of $CH_2(OCH_3)_2$ to CH_4 1:4, substrate temperature 850 °C, filament temperature

2100–2150 °C, filament-substrate distance 8 mm, and deposition time 15 h, under which BDD films with well-defined diamond features could be successfully deposited on Ti substrates with sufficient adhesion. These Ti/BDD electrodes had high electrochemical stability. More details of the preparation procedure can be found elsewhere [45, 46].

The Ti/SnO₂-Sb₂O₅ electrode was prepared using a standard thermal decomposition method. The dimensions of this electrode were 25 mm × 24 mm × 1.6 mm. Prior to coating, the Ti substrate underwent sandblasting, tap water washing, ten minutes of ultrasonic cleaning in deionized water, 2 min of etching in boiling 37% hydrochloric acid, and another ten minutes of ultrasonic cleaning in deionized water. After pretreatment, the Ti substrate was first brushed at room temperature with the precursors which had a molar ratio of Sb:Sn=1.5:98.5 using a mixture of iso-propanol and concentrated hydrochloric acid as solvents, dried at 80 °C for 5 min to allow solvents to vaporize, and then baked at 550 °C for 5 min. This procedure was repeated about 20 times. Finally the electrode was annealed at 550 °C for 1 h. The total oxide loading of the prepared electrodes was 15 g m⁻². More details of the preparation procedure can be found elsewhere [47, 48].

2.3. Cyclic voltammetric behavior

Cyclic voltammetric behavior was investigated in 0.5 M H₂SO₄ solution with a standard three-electrode cell (RDE0018, EG&G) and a potentiostat/galvanostat (PGSTAT 100, Autolab, Netherlands). Pt wire was used as a counter-electrode, and Ag/AgCl/saturated KCl (0.222 V vs NHE) with a Luggin capillary as a reference-electrode. The resistances between the working electrode and the Luggin capillary were measured using the frequency response analyzer of the potentiostat/galvanostat. The solution ohmic drops were compensated. Solutions were purged before electrochemical experiments with nitrogen gas.

2.4. Pollutant oxidation and accelerated life tests

The experimental set-up is schematically shown in Figure 1. The electrochemical reactor had dimensions of 130 mm in height and 30 mm in diameter, and was operated in a batch mode. Temperature was controlled at 30 °C using a water bath.

Accelerated life tests devised following Hutchings and coworkers [49] were used to assess electrode stability. The tests were conducted in 3 M H₂SO₄ solution at 50 °C. The working electrode was installed on a Ti holder. Pt wire was used as a counter electrode, and Ag/AgCl/saturated KCl served as a reference electrode. A DC power supply (PD110-5AD, Kenwood, Japan) was used to provide a constant current density of 10000 A m⁻². The potential of the working electrode was periodically monitored. Due to generation of a large amount of bubbles, usage of a Luggin capillary was

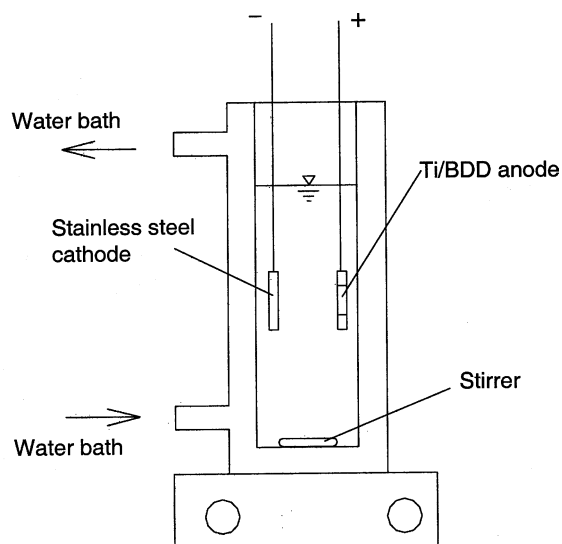


Fig. 1. Electrochemical reactor.

impossible. However, the reference electrode was placed as close as possible to the working electrode to reduce the solution ohmic drop.

3. Results and discussion

3.1. Cyclic voltammetric behavior

It was observed that the voltammogram shape changed gradually for the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$ electrode during scanning. Consistent voltammograms were not obtained until scanning for about 200 cycles. The situation for the Ti/BDD electrode was different. A relatively large voltammetric current was detected initially. The voltammetric current decreased quickly, however. After

about 20 cycles, the voltammogram shapes became identical. This indicates that the Ti/BDD electrode may have higher electrochemical stability. Figure 2 compares the voltammograms obtained on the Ti/BDD and $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$ electrodes after reaching steady state. The $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$ has an onset potential of 1.9 V vs NHE for O_2 evolution, consistent with the literature data [50]. In contrast, the onset potential for O_2 evolution on the Ti/BDD electrode is 2.7 V vs NHE, 0.8 V higher than that obtained on the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$ electrode. It should be noted that high onset potential for O_2 evolution is desired because O_2 evolution is a side reaction in the process of anodic oxidation of pollutants. The much higher onset potential for O_2 evolution suggests that the Ti/BDD electrode may have much higher current efficiency than the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$ electrode for pollutant oxidation.

3.2. Activity

In order to compare the activity between Ti/BDD and $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$ electrodes, oxidation of phenol, which is among the most toxic organic pollutants present in many industrial effluents, was investigated first. Figure 3 shows the COD variations with charge loading. It was found that both electrodes could mineralize phenol. But the Ti/BDD electrode was more effective than the $\text{Ti/SnO}_2\text{-Sb}_2\text{O}_5$ electrode. At a charge loading of 4.85 A h L^{-1} , the former electrode reduced COD from initial 1175 mg L^{-1} to 40 mg L^{-1} . In contrast, the latter electrode could only reduce COD to about 500 mg L^{-1} at the same charge loading. In an attempt to lower COD to a level of 40 mg L^{-1} , a twofold charge loading was required.

During the experiments, it was observed that a small amount of brown polymeric film was formed on the

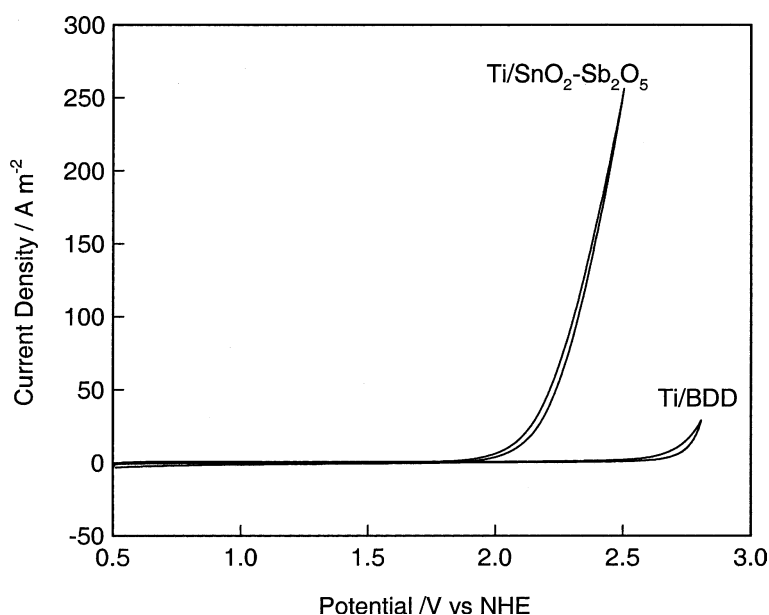


Fig. 2. Comparison of cyclic voltammograms obtained on different electrodes after reaching steady states Ti/BDD and $\text{Ti/Sb}_2\text{O}_5\text{-SnO}_2$.

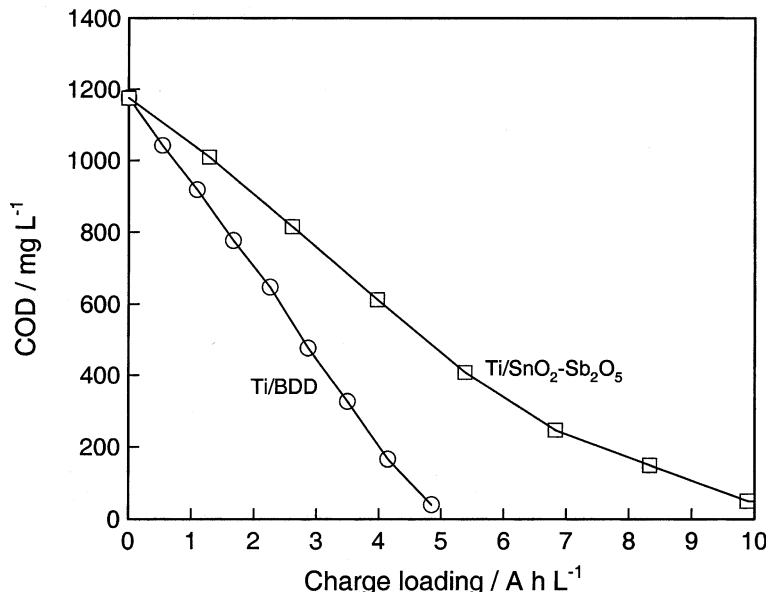


Fig. 3. Oxidation of 500 mg L⁻¹ phenol. Current density 100 A m⁻², reaction temperature 30 °C, Na₂SO₄ 1500 mg L⁻¹.

electrode surfaces. This is not a new finding, but a common phenomenon. Many researchers have observed polymeric film formation in oxidizing phenol on different electrodes [51–53]. A reaction mechanism via phenate anions with the formation of a polyoxyphenylene film was proposed [51]. Comninellis and Pulgarin [52] reported that the polymeric film formed had good electrical conductivity. They also pointed out that the formation of the polymeric film depended strongly on the experimental conditions. Alkaline media (pH > 9), low current densities (<300 A m⁻²), high temperatures (≥50 °C) and high phenol concentrations (≥50 mM) favored film formation.

The decay of electrode activity is believed to be one of the major problems of the anodic oxidation. Figure 4 compares the reproducibility of oxidizing phenol on Ti/BDD and Ti/SnO₂-Sb₂O₅ electrodes. It can be seen that the activity of the Ti/SnO₂-Sb₂O₅ electrode worsened rapidly. A new Ti/SnO₂-Sb₂O₅ electrode reduced COD from initial 1175 to 50 mg L⁻¹. The same electrode, however, could only reduce COD to about 220 mg L⁻¹ after operation for 20.6 h in five experiment cycles. It is encouraging to find that the situation for the Ti/BDD electrode is rather different. Even after 86.6 h in nine cycles, the electrode still showed high activity for phenol oxidation, further demonstrating much better

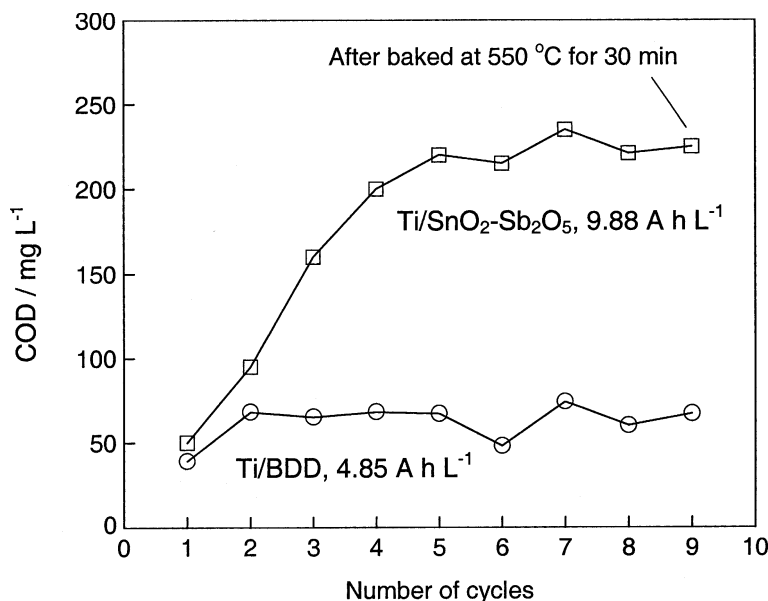


Fig. 4. Reproducibility comparison of oxidation of 500 mg L⁻¹ phenol on Ti/BDD and Ti/Sb₂O₅-SnO₂. Initial COD 1175 mg L⁻¹, current density 100 A m⁻², temperature 30 °C.

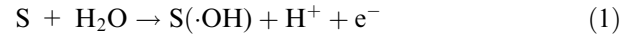
electrochemical performance of Ti/BDD than that of Ti/SnO₂-Sb₂O₅.

The loss of electrode activity is usually attributed to the formation of the polymeric film on the electrode surface. In order to verify this point, the Ti/SnO₂-Sb₂O₅ electrode was baked at 550 °C for 30 min after used for 33 h in eight cycles. It was found that the electrode activity was not improved at all on the 9th cycle, however. This indicates that the loss of the Ti/SnO₂-Sb₂O₅ electrode activity is not a consequence of formation of a polymeric film on the electrode surface, but probably due to the change in SnO₂-Sb₂O₅ crystal structure. To recover the Ti/SnO₂-Sb₂O₅ electrode activity, other attempts including soaking the electrode in acetone, hexane, and hot 10% NaOH solution (90 °C) for 10–30 min were also tried. None of these efforts was successful. Therefore, it is believed that the loss of the Ti/SnO₂-Sb₂O₅ electrode activity is irreversible. Structurally, diamond is highly inert at ambient temperature. This important feature enables the BDD film to maintain its high activity for pollutant oxidation. Actually, Perret and co-workers [35] have reported that Ti/BDD electrodes could be used for 350 h and more than 65 experiment cycles with no deterioration of activity.

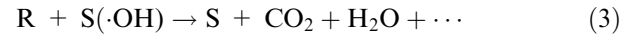
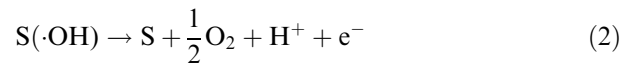
It is well known that reactive dyes are very resistant to oxidation. Most reactive dyes are biologically refractory organic compounds. In order to compare the activity of Ti/BDD and Ti/SnO₂-Sb₂O₅ electrodes further, oxidation of various reactive dyes was investigated. The results are listed in Table 1. Despite the fact that the Ti/SnO₂-Sb₂O₅ electrode could mineralize phenol, its efficiency in oxidizing reactive dyes was very poor. After treatment, COD was only reduced from 402–980 mg L⁻¹ to 216–712 mg L⁻¹. The current efficiencies were 18.9–47.7%. The situation for the Ti/BDD electrode was rather different. Like phenol, reactive dyes could also be mineralized on this electrode effectively. After treatment, the residual COD concentrations were

only 8–93 mg L⁻¹, with current efficiency being as high as 51.0–90.2%. Obviously, the Ti/BDD electrode is much more active than the Ti/SnO₂-Sb₂O₅ electrode.

The activity difference of oxidizing pollutants on different electrodes can be partially explained by the difference in the hydroxyl radical concentrations at different electrode surfaces (S). It has been well established that anodic oxidation of organic pollutants in the potential region of O₂ evolution on the BDD and SnO₂-Sb₂O₅ electrodes involve generation of adsorbed hydroxyl radicals, S(·OH) [50, 54]:



S(·OH) can then either be further oxidized to generate O₂ gas, or react with pollutants (R) to produce CO₂, H₂O, etc:



Usually, reaction (1) is easy, and thus not a rate-determining step. The activity of an electrode is highly dependent on the rate of reaction (2). Since the Ti/BDD electrode has much higher overpotential for O₂ evolution than the Ti/SnO₂-Sb₂O₅ electrode as shown in Figure 2, the rate of reaction (2) on the Ti/BDD electrode should be much lower than on the Ti/SnO₂-Sb₂O₅ electrode. This leads to a more significant accumulation of the hydroxyl radicals on the Ti/BDD electrode surface, and therefore the Ti/BDD electrode can oxidize pollutants more effectively than the Ti/SnO₂-Sb₂O₅ electrode under the same conditions. Moreover, diamond is well known to have weak adsorption properties due to its inert surface [55]. Therefore, the hydroxyl radicals produced on the Ti/BDD electrode are very weakly adsorbed and

Table 1. Comparison of Anodic Oxidation of Various Reactive Dyes on Ti/BDD and Ti/SnO₂-Sb₂O₅ Electrodes under Current Density 100A m⁻², Temperature 30 °C, Volume 25 mL, Initial Dyes Concentration 1000 mg L⁻¹, and Initial pH 4.70–6.73

Dyes	Charge/A h L ⁻¹	Initial COD/mg L ⁻¹	Residual COD/mg L ⁻¹		Current efficiency/%	
			Ti/BDD	Ti/SnO ₂ -Sb ₂ O ₅	Ti/BDD	Ti/SnO ₂ -Sb ₂ O ₅
Cibacron yellow HW200	3.52	737	28	526	67.5	20.1
Cycafix yellow FLN250	3.02	610	31	386	64.2	24.8
Cycafix Navy-blue F2B	2.77	659	64	453	72.0	24.9
Monozol black SGRN	2.52	710	78	451	84.0	34.4
Monozol blue BRF-150	2.52	634	71	466	74.8	22.3
Monozol red F3B150	2.39	654	72	425	81.6	32.1
Monozol T-blue HFG	4.03	980	93	712	73.7	22.3
Monozol yellow F3R150	2.52	667	74	423	78.8	32.4
Procion blue HE-RD	3.02	902	89	551	90.2	38.9
Reactive blue R	2.90	803	61	390	85.7	47.7
Reactive red HE-7B	2.52	402	19	216	51.0	24.7
Samafix red S-3B	2.52	607	38	370	75.6	31.5
Samafix yellow S-3R	2.52	440	50	277	51.8	21.7
Unicion green S6B	4.03	711	8	484	58.4	18.9
Unicion red S-3BF80	2.27	589	66	381	77.2	30.7

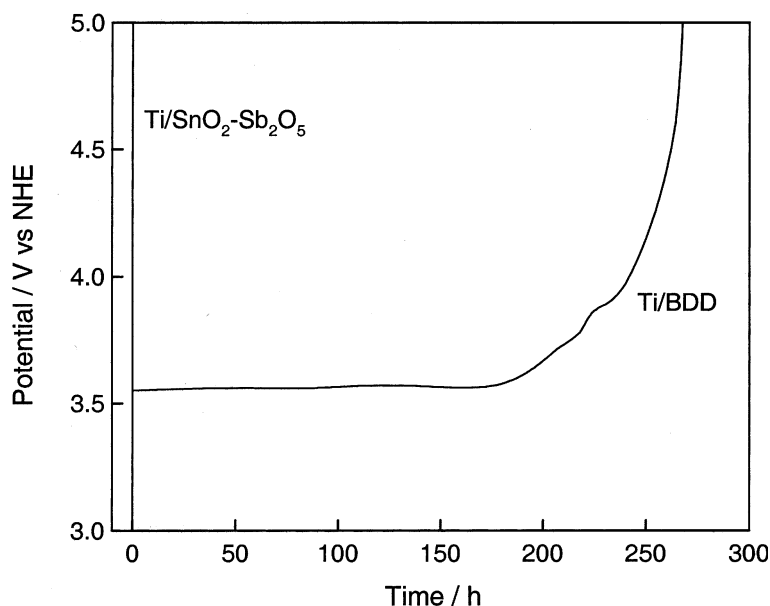


Fig. 5. Potential variation with time in accelerated life tests performed in 3 M H₂SO₄ solution under 10 000 A m⁻² at 50 °C.

accordingly are very reactive in pollutant oxidation. In contrast, Sb₂O₅-SnO₂ is hydrated. Therefore, the hydroxyl radicals produced on the Ti/Sb₂O₅-SnO₂ electrode are expected to be more strongly adsorbed and are less reactive towards pollutant oxidation.

3.3. Electrochemical stability

Figure 5 compares the potential changes with time in the accelerated life tests for two different electrodes. The Ti/SnO₂-Sb₂O₅ electrode demonstrated a sharp increase in potential. In fact, this electrode failed permanently within several seconds, indicating its poor electrochemical stability. The low durability of the Ti/SnO₂-Sb₂O₅ electrode in the accelerated life test was not surprising. Correa-Lozano and co-workers [56] reported that a Ti/SnO₂-Sb₂O₅ was damaged after running for about 12 h at a current density of 1000 A m⁻², ten times lower than that used in the present study. Lipp and Pletcher [57] investigated the long-term stability of a Ti/SnO₂-Sb₂O₅ electrode at a constant potential. It was found that current density decreased gradually from an initial value of 200 to 60 A m⁻² after running for about 1000 h.

The situation for the Ti/BDD electrode was rather different. The potential remained almost unchanged for about 180 h, then increased gradually. Rapid potential increase was observed in the last 20 h due to the BDD film detachment. The service life of an electrode is defined as the operational time at which the potential increases rapidly to 5 V. Therefore, the Ti/BDD electrode had a service life of 264 h. It should be noted that the service life mentioned here were obtained in the accelerated life test performed in a 3 M H₂SO₄ aqueous solution at a current density as high as 10 000 A m⁻². The real service life of a Ti/BDD electrode will be much longer under normal operational conditions, usually with a current density <500 A m⁻². This is because the

service life increases significantly when the current density decreases. For example, the service life of IrO₂-based DSA[®] electrodes was about 25 times higher at 1600 A m⁻² than at 16 000 A m⁻² [58]. In addition, it was reported that Ti/RuO₂-TiO₂ electrodes could be used for only 18 h at 20 000 A m⁻² in 2 M HClO₄ plus 0.2 M NaCl solution, but when the current density was lowered to 5000 A m⁻², the service life increased to about 200 h [59]. Therefore, the Ti/BDD electrode is believed to be sufficiently stable for application at low current densities.

4. Conclusions

The performances of Ti/BDD and Ti/SnO₂-Sb₂O₅ were compared under the same conditions. Experimental results indicate that the former is a much better anode than the latter in terms of both electrochemical activity and electrode stability. The current efficiency for the Ti/BDD anode is over 50% for all the pollutants tested while that for Ti/SnO₂-Sb₂O₅ is always significantly below 50%. The Ti/BDD can mineralize phenol and reactive dyes while Ti/SnO₂-Sb₂O₅ works for phenol but not all the dyes. The Ti/BDD shows a reasonable service life. Repeated usage of a Ti/BDD anode does not show appreciable deterioration of its performance. A Ti/SnO₂-Sb₂O₅ anode, in contrast, only lasts a few seconds when the current intensity is increased to 10 000 A m⁻² in 3 M H₂SO₄.

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