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Anodic Materials with High Energy Efficiency for Electrochemical Oxidation of Toxic Organics in Waste Water

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1. Introduction

With the development of human society, discharge of toxic organics in industrial waste water increased sharply. It is difficult to treat these types of waste water efficiently by traditional bio-process to meet the more critical discharge standard. Advanced oxidation processes (AOPs) attracted more and more attention as efficient methods to remove the toxic organics from waste water. Compared with other AOPs, electrochemical oxidation process was considered as an effective and environmental friendly process due to its simplicity in operation, robustness in system configuration, strong oxidizing ability, reliable performance for a wide variety of toxic organics and chemical reagents free.

The electrochemical system is basically composed of anode, cathode, electrolyte and cell. Oxidation occurs on the anode while reduction occurs on the cathode simultaneously. For the electrochemical oxidation process, the toxic organics oxidation can be performed in several different ways, including direct and indirect oxidation, which are shown in Fig. 1. The oxidation mechanisms are generally observed to be influenced by the electrode material, the electrolyte composition and experimental conditions.

In direct electrolysis, the toxic organics are oxidized directly on the anode surface after its adsorption without involvement of any other substances except the electrons, as shown in Fig. 1(a).

Direct electrochemical oxidation is theoretically possible at low potentials, before oxygen evolution occurs. But the reaction rate is usually low and the anodic potential has to be controlled at a constant lower value to avoid the oxygen evolution reaction. At this low potential, the formation of polymer layer on the anode surface will be accelerated and the anode will lose its activity. This deactivation actually depends on the adsorption properties of the anode surface and the properties of the organic substrates. Aromatic compounds such as phenol (Foti et al., 1997; Gattrell & Kirk, 1993), chlorophenols (Rodgers et al., 1999; Rodrigo et al. 2001), naphthol (Panizza & Cerisola, 2003; Panizza & Cerisola, 2004) and pyridine (Iniesta et al., 2001a) were reported to form polymer layer on anode surface easily.

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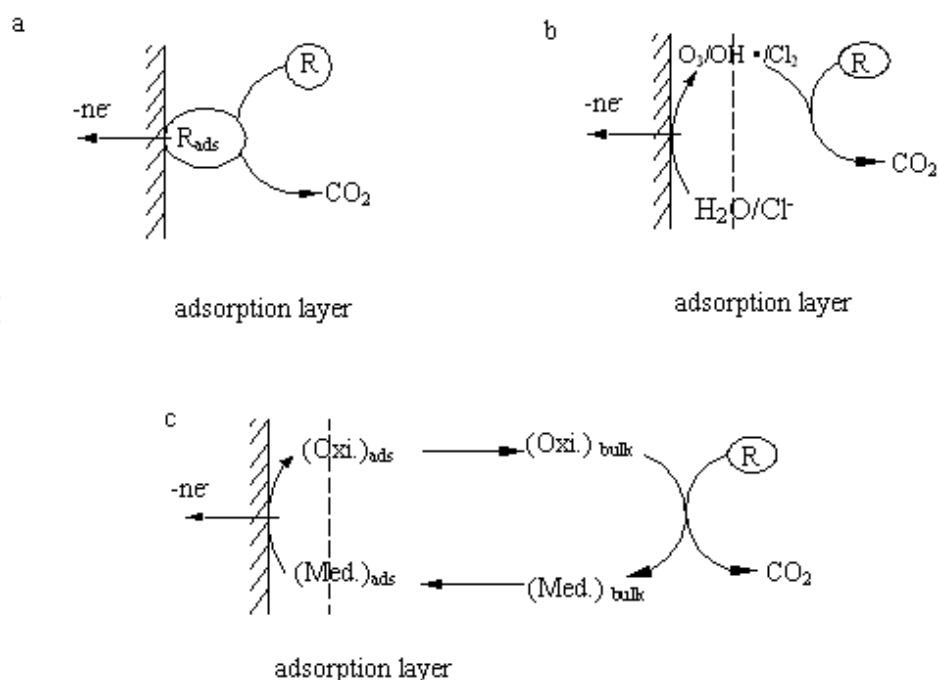


Fig. 1. Scheme of the electrochemical processes for the oxidation of organics: (a) direct electrolysis; (b) irreversible indirect electrolysis; (c) reversible indirect electrolysis

In order to accelerate the organics oxidation rate, in practical applications, higher oxidation potential on anode is needed and other side reactions like oxygen evolution occur. Thus another important mechanism usually accompanied with the organics electrochemical oxidation.

In indirect oxidation, the organic substrates do not donate electrons directly to the anode, but they would react with the active oxidants generated from the anode as showed in Fig. 1 b (irreversible) and c (reversible). In reversible process, the redox reagents are turned over many times and recycled. The redox couples can be metal ions such as $\text{Ag}^+/\text{Ag}^{2+}$ (Farmer et al., 1992), $\text{Co}^{2+}/\text{Co}^{3+}$ (Leffrang et al., 1995), $\text{Fe}^{2+}/\text{Fe}^{3+}$ (Dhooge & Park, 1983) or inorganic ions such as Cl^-/ClO^- (Comninellis & Nerini, 1995; Szpyrkowicz et al., 1995), Br^-/BrO^- (Martinez-Huitle et al., 2005). These redox couples can be added to or present in the waste water. In irreversible process, strong oxidants like ozone (Chen et al., 2010; Wang et al., 2006), chlorine (Panizza & Cerisola, 2003), hydrogen peroxide (Brillas et al., 1996; Brillas et al., 1995; Do & Chen, 1993) and hydroxyl free radicals (Johnson et al., 1999) etc. are generated and in-situ applied to mineralize the organic pollutants.

In the electrochemical system, the most important component is the anodic material. Different anodic materials show diverse effectiveness for toxic organics oxidation and the organics oxidation mechanisms are also different. According to the model developed by Comninellis (1994), anode materials are classified into two types as active and nonactive anodes. The active anodes such as carbon, graphite, platinum, iridium oxide and ruthenium oxide electrodes have lower oxygen evolution overpotential and are good electrocatalysts for oxygen evolution reaction. The nonactive anodes such as tin dioxide, lead dioxide, boron doped diamond electrodes have higher oxygen evolution overpotential and are poor electrocatalysts for oxygen evolution reactions. On active anodes, organics usually are partially oxidized while organics can be mineralized to carbon dioxide completely on

nonactive anodes. The electrochemical oxidation process usually consumes large amount of electrical energy. In order to increase the energy efficiency and decrease the energy consumption, people have paid much attention to investigate more effective anodic materials.

Till now, lead dioxide, tin dioxide and diamond as anodic materials have relative higher energy efficiency for electrochemical oxidation of toxic organics in waste water due to their high oxygen evolution potentials which can hinder the oxygen evolution side reaction in electrochemical oxidation process. These anodic materials have attracted much research interest and many research papers have been published. Also different preparation methods can affect the electrodes performance because the preparation methods have effect on the electrode morphology, crystal structure and other characteristics. Except the anodic materials mentioned above, $\text{Ta}_2\text{O}_5\text{-IrO}_2$, $\text{Nb}_2\text{O}_5\text{-IrO}_2$ and $\text{Pt-Ta}_2\text{O}_5$ etc. also are nonactive anodes and show good electrochemical properties. They may also have the potential to be used in electrochemical oxidation process. From the above mentioned considerations, it is necessary to summarize the efficient anodic materials for electrochemical oxidation of toxic organics.

In this work, the development in last decade of the anodic materials including lead dioxide, tin dioxide and diamond materials will be reviewed in detail from their preparation, structure characterization and performance. A few other anodic materials will also be introduced briefly.

2. Lead dioxide

Lead dioxide has a long history of use as anode for the oxidation of organics and ozone generation because of its good conductivity and large overpotential for oxygen evolution. Lead dioxide anodes also have a lower cost compared to those based on precious metals. Lead dioxide anode can be prepared with different phase structures, surface morphologies with different doping and preparation conditions. Thus this can contribute to the fundamental understanding of the relationship between the structure and catalytic properties, which is very important to all catalysis fields (Li et al., 2011). Pure lead dioxide is an odorless dark-brown crystalline powder which is nearly insoluble in water. It has two major polymorphs, alpha and beta, which occur naturally as rare minerals scrutinyite and plattnerite, respectively. The alpha form has orthorhombic symmetry, space group Pbcn (No. 60), Pearson symbol oP12 , lattice constants $a = 0.497 \text{ nm}$, $b = 0.596 \text{ nm}$, $c = 0.544 \text{ nm}$, $Z = 4$ (four formula units per unit cell). The symmetry of the beta form is tetragonal, space group P42/mnm (No. 136), Pearson symbol tP6 , lattice constants $a = 0.491 \text{ nm}$, $c = 0.3385 \text{ nm}$, $Z = 2$. The crystal structures of alpha and beta form are shown in Fig. 2.

2.1 The preparation of lead dioxide

Lead dioxide is usually prepared by anodic deposition method. Basically, the lead source exists as lead(II) salt in the aqueous electrolyte, while electrode substrate as anode, under an anodic current, lead dioxide will deposit on the anode. The mechanism for lead dioxide formation on anode is still not clear. Velichenko (1996) proposed a two steps mechanism. The first step is the formation of adsorbed hydroxyl free radicals and the second step is the hydroxyl free radicals reacting with lead(II) ions to form Pb(OH)^{2+} as intermediate. And soon the Pb(OH)^{2+} is further oxidized to PbO_2 .

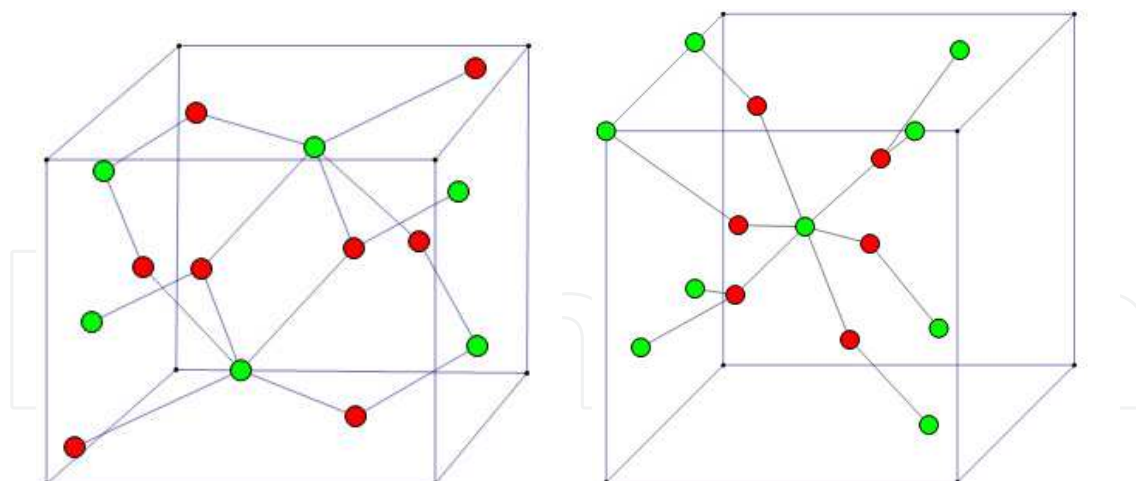


Fig. 2. The crystal structures for α -PbO₂ (left) and β -PbO₂ (right) (green dots represent Pb while red dots represent O)

The literature on the anodic deposition of lead dioxide is very extensive. And it is clear that the adhesion, surface morphology and ratio of alpha/beta form and catalytic activity can be influenced by substrate and its pretreatment process, dopant and its concentration, additives, depositing pH, depositing current density and potential, lead source and concentration and temperature etc. In order to improve lead dioxide anode performance including the activity and lifetime, people tried many different dopants, substrates and other techniques for the anodic deposition of lead dioxide. The earlier lead dioxide preparation was based on in situ oxidizing lead or lead alloy. This type of anode always suffered from continuous corrosion of the underlying lead substrate. It is only more recently that the stable lead dioxide can be anodically deposited on inert substrates such as titanium and carbon.

Though some academic publications employed Pt, Au (Chang & Dennis, 1991; Velichenko et al., 1995; Yeo et al., 1992), graphite (Munichandraiah & Sathyanarayana, 1987), tantalum (Tahar & Savall, 1999) or glassy carbon (González-García et al., 2002; Sáez et al., 2011a; Velayutham & Noel, 1991) as substrate for lead dioxide anode electro-deposition, titanium is mostly used as the lead dioxide electrode substrate because titanium has relative low cost, strong mechanical strength and good adhesion to the lead dioxide layer. Titanium as electrode substrate is usually pretreated in order to remove the existing titanium oxide layer, grease and other contaminants on the surface. The usually used pretreatment process may include sandblasting, alkaline degrease followed by etching in boiling oxalic acid or hydrochloric acid. After this pretreatment, the substrate is relative clean and rough and suitable for anodic depositing lead dioxide. With the clean and rough surface, the deposited lead dioxide layer may be attached strongly. In order to further improve the electrode, some interlayer is also applied to titanium substrate before lead dioxide deposition. This interlayer may be helpful to improve the electrode conductivity, stability and activity. The interlayers proposed include platinum (Devilliers et al., 2003), TiO₂/Ta₂O₅ (Ueda et al., 1995) and TiO₂/RuO₂ (Hine et al., 1984). Also some people proposed multi interlayers before catalyst layer applied. Ueda et al. (1995) employed a thermally formed oxide layer TiO₂/Ta₂O₅ attached to the substrate, which could improve the layers adhesion to the substrate. After the oxide interlayer, Ueda et al. employed another alpha lead dioxide layer between the oxide interlayer and catalyst layer because the alpha lead dioxide layer is stress

free and can prevent the corrosive electrolyte penetrating to the substrate to destroy the anode. Finally an active beta lead dioxide and tantalum oxide composite layer was employed as catalyst layer and a stable and active lead dioxide anode was achieved. Feng and Johnson (1991) and Mohd and Pletcher (2006) proposed that F doped lead dioxide interlayer could give good adhesion and stability, while Bi or Fe doped lead dioxide catalyst layer could give the desired electrocatalytic activity. Except employing the interlayers to enhance the adhesion and control the inside stress of the lead dioxide anode, some soluble organic additives were also applied in the electroplating bath. Munichandraiah and Sathyanarayana (1987) found that Teepol could improve the adherence while creating a higher surface area. Ghaemi et al. (2006) and Wen et al. (1990) found that by adding Triton X-100 to the electroplating bath, the adhesion between the substrate and catalyst layer was improved, so as the mechanical strength and oxygen evolution potential. Adding gelatin and sodium dodecylsulfonate to the electroplating bath could modify the electrode morphology and decrease the beta lead dioxide content (Wen et al., 1990). Polyvinyl pyridine could be used to control both the morphology and crystallite size (Ghasemi et al., 2007). Other additives such as tetraalkylammonium ions were also applied in lead dioxide anode preparation process (Ghanasekaran et al., 1976; Pletcher & Wills, 2004). Low et al. (2009) reported that a highly reflective lead dioxide electrode could be prepared by adding hexadecyltrimethylammonium chloride or bromide to the electroplating bath.

In last decades, people tried different dopants to improve the lead dioxide coated anode characteristics and large improvements were achieved without any doubt. Generally, the doped lead dioxide anode was prepared by simply adding doping elements into the electroplating bath. And the effective dopants are generally F⁻, Bi³⁺, Fe³⁺, Co²⁺ etc. F⁻ and Fe³⁺ doping as mentioned above, could enhance the adhesion and mechanical strength (Feng & Johnson, 1991; Mohd & Pletcher, 2006). While Bi³⁺ (Feng & Johnson, 1991; Iniesta et al., 2001c; Liu et al., 2008b; Mondal et al., 2001; Mohd & Pletcher, 2006; Yeo et al., 1989) and Co²⁺ (Andrade et al., 2008; Velichenko et al., 2002) were reported to enhance the organics oxidation and reduce the electrode fouling by organics. During the organics oxidation, it was suggested that the dopants promote the formation of adsorbed OH radicals by increasing the oxygen vacancies concentration in lead dioxide lattice. In addition, preparation and properties of the rare earth doped lead dioxide were seldom reported. Kong et al. (2007) reported that the crystal structure of the PbO₂ electrodes was influenced by doping with different rare earth oxides. The presence of Er₂O₃ and La₂O₃ in the PbO₂ films could enhance the direct anodic oxidation, which was helpful to mineralize organic wastes. Yang et al. (2010) reported that Nd, Sm, Gd, Ce doping did not change the crystal form of PbO₂ electrodes but improve the crystal purity of beta-PbO₂. SEM results indicated that the morphology of the electrode surface had changed at different degrees. The lifetime and activity were improved by rare earth doping.

Nanostructured material is a hot topic in modern research because nano-material usually has the particles size in nano meter scale and relative large surface area. So people also paid effort to prepare lead dioxide anode with nano-structure. The nano-structured lead dioxide anode usually was prepared by employing nano-structured template as deposition substrate. Inguanta et al. (2008) and Perret et al. (2009) proposed electrodepositing lead dioxide onto commercial anodic alumina membranes with mean pore diameter of c.a. 210 nm. The electroplating was conducted in a lead nitrate solution bath and after the

deposition, the alumina was dissolved in sodium hydroxide to achieve free standing lead dioxide nanowire clusters. Bartlett et al. (2002) deposited lead dioxide onto self-assembled polystyrene microspheres and then the polystyrene was dissolved out by an organic solvent to get a highly ordered lead dioxide nano-structure. Tan et al. (2011) prepared nano lead dioxide by employing self-organized TiO_2 nanotube arrays as substrate.

In general, composites in metal electroplating have been used to improve the strength, wear resistance, corrosion resistance, and catalytic activity. Thus people also utilized this composites technology to prepare lead dioxide anode. PTFE and polypyrrole have good hydrophobic property and they are applied to introduce hydrophobicity and assist the gases release, aid the interaction between the organic molecules and electrode surface (Hwang & Lee, 1996; Ho & Hwang, 1994; Tong et al., 2008; Yoshiyama et al., 1994; Zhao et al., 2010). The PTFE and polypyrrole may also have the function of reducing the coating films inside stress thus to improve the electrode stability. Fu et al. (2010) reported that PbO_2/PVA composites electrode also had excellent electrocatalytic activity and longer life time and higher corrosion resistance due to the addition of PVA deducing the lead dioxide particle size and increasing the conductivity. Binh et al. (2011) very recently tried to prepared PbO_2/PANI composite anode. People also used composites materials like $\text{PbO}_2/\text{RuO}_2$ (Musiani et al., 1999; Bertoncello et al., 1999), $\text{PbO}_2/\text{Co}_3\text{O}_4$ (Musiani, 1996; Bertoncello et al., 1999), $\text{PbO}_2/\text{IrO}_2$ (Musiani, 2000) to get a more stable and active anode for oxygen evolution. More recently, the $\text{PbO}_2/\text{TiO}_2$ composites have attracted considerable attention due to its potential application in photo electrocatalytic oxidation of organic waste in wastewater (Velichenko et al., 2009). Li et al. (2006a; 2006b) reported the electrochemically assisted photocatalytic degradation of toxic organic waste on composites $\text{PbO}_2/\text{TiO}_2$ photoelectrode.

Except the above mentioned, anodic deposition of lead dioxide was attempted to be assisted by ultrasound waves (González-García et al., 2002; Sáez et al., 2011b; Ghasemi et al., 2008). The results indicated that the ultrasound could improve the prepared lead dioxide stability, adhesion and mechanical strength.

2.2 Lead dioxide anode application in waste water treatment

Lead dioxide anode has wide applications in oxygen evolution, ozone generation, lead acid batteries, manufacturing fine chemicals and water and waste water treatment. For waste water treatment, due to its relative high cost compared to the most favorable biological process, the electro oxidation process was usually used to oxidize organic wastes which are toxic and resistant to biological treatment. These organic compounds usually include phenol (Andrade et al., 2008; Tahar & Savall, 1999), aniline (Hmani et al., 2009), benzoquinone, chlorinated phenol (Cao et al., 2009; Tan et al., 2011), nitrophenol (Liu et al., 2008a), naphthol (Panizza & Cerisola, 2003; Panizza & Cerisola, 2004), cyanide (Hine et al., 1986), benzene (Hamza et al., 2011), cresols (Flox et al., 2009), chloranilic acid, indoles, tannic acid, 1,2-dichloroethane, herbicides (Panizza et al., 2008), pesticides (Youssef et al., 2010), surfactants (Weiss et al., 2006) and dyes.

Borras et al. (2003) studied the initial stages of oxidation of aqueous solutions of p-chlorophenol (p-CP) and p-nitrophenol (p-NP) on Bi-doped PbO_2 electrodes. Benzoquinone and aliphatic acids were identified as the primary oxidation intermediates. Oxidation of benzoquinone was found to be the slow step during the early stages of the electrochemical combustion process. The effect of competing adsorption of p-CP and p-NP on Bi- PbO_2 was

also examined, and the presence of p-NP in solution was found to inhibit the p-CP oxidation during concurrent oxidation of both phenols.

Liu et al. (2008a; 2008b; 2009) studied the electrocatalytic oxidation of o-nitrophenol (o-NP), m-nitrophenol (m-NP) and p-nitrophenol (p-NP), dinitro-phenol and trinitro-phenol at Bi-doped lead dioxide anode in acid medium by cyclic voltammetry and bulk electrolysis. The results of voltammetric studies indicated that these nitrophenol isomers were indirectly oxidized by hydroxyl radicals in the solutions. Molecular configuration including the electron character and hydrogen bonds of NPs significantly influenced the electrocatalytic oxidation of these isomers. The efficiency for electrocatalytic oxidation of NPs lay in the order of p-NP > m-NP > o-NP, while 2,6-dinitrophenol > 2,5-dinitrophenol > 2,4-dinitrophenol > 2,4,6-trinitrophenol. Hydroquinone, catechol, resorcinol, benzoquinone, aminophenols, glutamic acid and maleic acid and oxalic acid had been detected as soluble products during the electrolysis of NPs.

Awad and Abo (2005) investigated the electrocatalytic degradation of Acid Blue and Basic Brown dyes from artificial wastewater on lead dioxide anode in different conductive electrolytes. It was shown that complete degradation of these dyes was dependent primarily on type and concentration of the conductive electrolyte. The highest electrocatalytic activity was achieved in the presence of NaCl. The possibility of electrode poisoning as a result of growth of adherent film on the anode surface or production of stable intermediates not easily further oxidized by direct electrolysis in H_2SO_4 might be accountable for the poor performance observed in this conductive electrolyte. Optimizing the conditions that ensure effective electrochemical degradation of Acid Blue and Basic Brown dyes on lead dioxide electrode necessitated the control of all the operating factors.

The above mentioned studies, however, were conducted in lab with controlled pH and low current density, which were seldom used in real waste water treatment plants. Only few papers dealt with real waste water such as landfill leachate (Cossu et al., 1998), tannery waste, dye plant effluents etc (Ciriaco et al., 2009). However, due to the complex composition of the real waste water, the mechanism for organic compounds oxidation was difficult to discuss. Before the technology could be practically use, a lot of research work including the bench scale and pilot scale test should be done.

3. Tin dioxide

Tin dioxide is a well known n-type semiconductor with a wide band gap ($>3.7\text{eV}$). It crystallizes with the rutile structure, also called cassiterite structure, which belongs to the space group D_{4h} ($P4_2/mnm$), with a unit cell containing two tin and four oxygen atoms (Fig. 3).

In Fig. 3, the oxygen atoms are placed approximately at the corner of regular octahedron, and tin atoms are placed approximately at the corners of regular octahedron, and tin atoms are located approximately at the corners of an equivalent triangle. The lattice parameters are $a=b=0.4737\text{ nm}$, $c=0.3185\text{ nm}$. The d-spacing for $\text{SnO}_2(110)$ and $\text{SnO}_2(101)$ is 0.3350 nm and 0.2643 nm , respectively. Due to its advantageous electrical, electrochemical and optical properties, SnO_2 has been widely used in various fields such as gas sensors, solar cells and electrode material for electrolysis and lithium ion batteries.

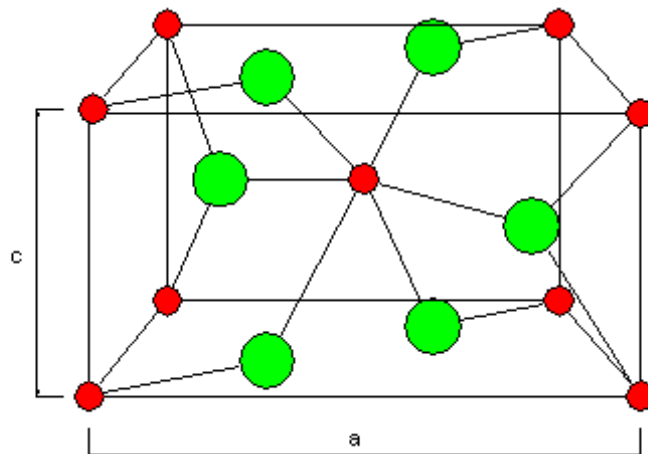


Fig. 3. The cassiterite crystal structure for tin dioxide lattice (small dots are Sn atoms and larger dots are O atoms)

3.1 The preparation of tin dioxide

Tin dioxide as an anode material is usually prepared on a substrate, which can support the tin dioxide active layer. The mostly used substrate is titanium, the same as lead dioxide anode used. Also the titanium shall be pretreated before active layer coating. The pretreatment process is also the same as described in section 2.1, that is sandblasting, degreasing by alkaline or acetone and boiling in acid. However, tin dioxide layer can not be prepared by anodic deposition. It is prepared usually by thermal decomposition method, in which tin salt can be oxidized to tin oxide in air at high temperature. According to the coating solution preparation method, the thermal decomposition method can be classified into dip-coating pyrolysis and sol-gel dip coating method.

3.1.1 The dip-coating pyrolysis method

In this method, the coating solution is directly prepared from metal salt. That is to dissolve the metal chloride into alcohol solvent. The alcohol solvent can be absolute ethanol, isopropanol, butanol or the mixture of them. If any dopants needed, the doping elements shall also be dissolved into the mixture. In order to get a uniform solution, a few drops of hydrochloric acid are usually added to avoid the hydrolysis of the metal salts. Then the pretreated titanium substrate can be dipped into the coating solution and then a liquid film formed on the titanium surface. Then the substrate is moved to an oven to dry at 80-100 °C for about 10 min to evaporate the solvent. After then, the titanium substrate is moved to a furnace, in there, the coated tin salt is transformed to tin oxide under high temperature. This procedure, as illustrated in Fig.4, is repeated for 15~30 times until a required tin oxide film thickness achieved.

The dip-coating pyrolysis procedure is relative simple, easy operating and cost effective. However, this method may also introduce non-uniform tin oxide layer with cracks and islands structure due to the inside stress deduced from the thermal treatment. The typical antimony doped tin dioxide electrode surface morphology is shown in Fig. 5. This structure may contribute to the poor stability.

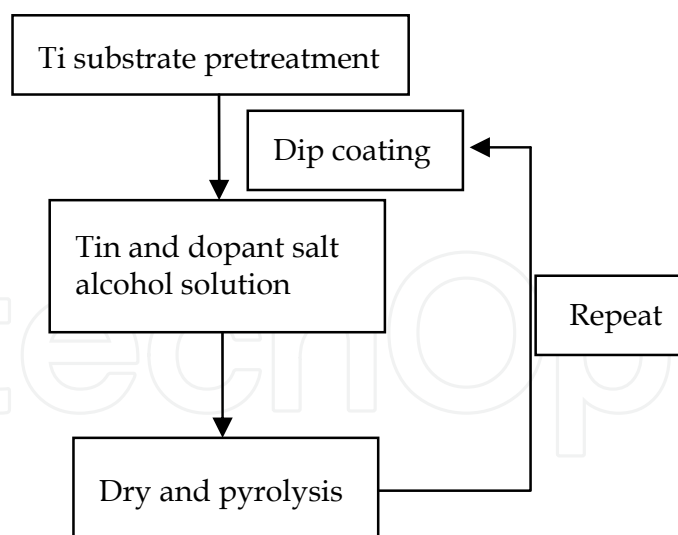


Fig. 4. The illustration for the tin oxide electrode preparation procedure

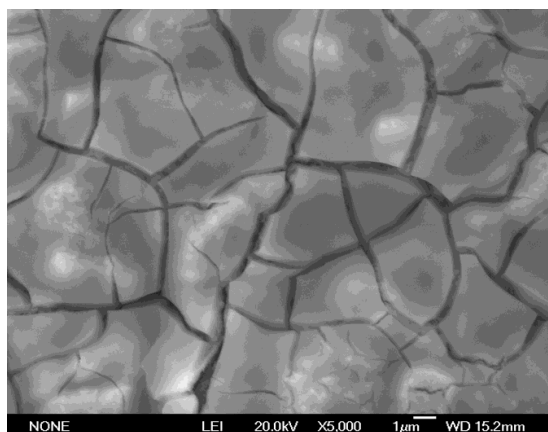


Fig. 5. Typical SEM image of antimony doped tin dioxide electrode prepared by dip-coating pyrolysis

In this procedure, the coating solution composition and pyrolysis temperature are key factors to affect the electrode activity. From the extensive report on doped tin dioxide electrode preparation, the optimized pyrolysis temperature usually lies in the range of 500-600 °C (Comninellis & Chen, 2010). The antimony is the mostly used dopant because its higher valence (+5) can introduce more oxygen vacancies in the tin dioxide lattice, which can improve the electrode conductivity and introduce more active sites for electrochemical oxidation. Also Sb^{5+} has the similar ionic radius, which can facilitate higher dopant concentration in the lattice. However, the optimized Sb doping concentration varied greatly (in the range between 1.6%-10% atomic) among different research groups (Vicent et al., 1998; Montilla et al., 2002; Montilla et al., 2004a; Montilla et al., 2004b). This was possible on one hand because people usually used the atomic percent in the coating solution, the final Sb concentration in the electrode was not determined accurately. On the other hand, the details of the preparation procedure may be different, such as the drying time and temperature, heating times and durations etc. which would affect the electrode performance even with the similar doping levels.

3.1.2 Sol-gel dip coating method

In order to overcome the shortages derived by direct pyrolysis method, sol-gel dip coating method was developed to prepare tin dioxide electrode. Actually, the sol-gel dip coating method is not a new concept in material chemistry. It has wide application in panel display manufacturing, nano materials preparation etc. In this technique for tin dioxide electrode preparation, the similar Ti substrate pretreatment is needed, while the coating solution is colloidal rather than an alcoholic solution.

The colloidal can be achieved both from inorganic metal salt or organic metal compounds. In a typical colloidal preparation procedure using inorganic metal salt as precursor, ammonia is added to the inorganic salt solution to facilitate the hydrolysis of metal salts. After hydrolysis, the colloidal is washed to remove the chloride ions, which is believed to be harmful to the electrode stability. Then the colloidal with water as solvent is heated up to 80 °C to finish the transformation from metal hydroxide to metal oxide and facilitate the doping ions into the tin oxide lattice. On the completion of hydrolysis and doping, the colloidal's color is becoming deep from yellow (lower Sb concentration) to grey (higher Sb concentration). In order to get a more uniform sol, some additives such as oxalic acid or polyethylene glycol can be added into the colloidal solution.

By coating the present colloidal solution on titanium followed high temperature heating for many times, the prepared electrode showed relative smooth and uniform surface structure. A typical SEM image of antimony doped tin dioxide electrode prepared by sol-gel dip coating method is showed in Fig. 6.

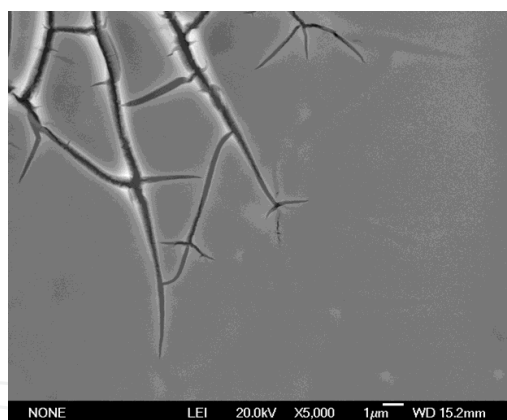


Fig. 6. SEM image of antimony doped tin dioxide electrode prepared by sol-gel dip coating method

From Fig. 6, the relative smooth surface and fewer cracks may prevent the corrosive electrolyte penetrating inside the catalyst layer, thus enhance the electrode stability. In another hand, the free contamination from chloride ions in the electrode may retard the hydration of the oxide layer and also contribute to a longer lifetime. Also in sol-gel dip coating method, the dopants concentration is easily controlled. Thus this technique attracts more and more attention in tin dioxide electrode preparation, though it suffers from the preparation of colloidal solution.

Except the above mentioned preparation method, people also attempted to prepare tin oxide electrode by electroplating tin metal or tin alloy onto titanium, followed by an oxidation

process in oven with air. In a typical electroplating procedure for antimony doped tin dioxide electrodes, the cleaned Ti substrate was first cathodic deposited in acidic solution containing Sn^{2+} and followed in citric acid solution containing Sb^{3+} with the same current density at room temperature. The metal ions (Sn^{2+} , Sb^{3+}) were reduced to metal alloy (SbSn) on the cathode. Repeat the electroplating procedure 3-5 times to get a thick metal alloy layer. Finally, the electrodes were calcined at high temperature for 3 h to obtain the Sb-SnO₂/Ti electrodes.

Except the preparation techniques, people also tried a lot of dopants to improve the tin oxide electrode activity. Except the above mentioned antimony dopant, Pt/Sb co-doped tin dioxide electrode was prepared and reported to have longer lifetime (Vicent et al., 1998). Berenguer et al. (2009) found that Ru and Pt co-doped tin dioxide electrode had better electrocatalytic activity for oxygen evolution. It was reported that with trace amount of nickel and antimony doped tin dioxide electrode showed promising applications for anodic oxidation and the current efficiency for ozone generation could reach up to 50%, which was much higher than that on lead dioxide (Christensen et al., 2009; Wang et al., 2005). In order to improve the adhesion and stability, people also tried to apply interlayer between the substrate and the top active layer. Debiemme-Chouvy et al. (2011) prepared conductive SnO₂ films deposited on a glass substrate by the spray pyrolysis technique. In order to improve the electrochemical behaviour of the SnO₂ films, conductive F-doped layer was first deposited followed by the deposition of a Sb-doped layer to form a bi-layer film. Ding et al. (2010) introduced a Sb doped tin dioxide inter-layer onto a titanium using electrodeposition method followed by coating its surface using thermo-decomposition procedures.

3.2 Tin dioxide anode application in waste water treatment

Extensive research indicates that tin dioxide and doped tin dioxide electrode has good activity toward organics degradation (Comninellis & Vercesi, 1991; Comninellis & Pulgarin, 1993; Houk et al., 1998; Stuki et al., 1991; Steve et al., 1999; Polcaro et al., 1999; Vicent et al., 1998). Generally, the organic waste is similar to those being treated by lead dioxide, which are toxic and resistant to biological treatment.

Houk et al. (1998) evaluated electrochemical incineration of benzoquinone in aqueous media using a quaternary metal oxide electrode, which is a Ti or Pt anode coated with a film of the oxides of Ti, Ru, Sn and Sb. They concluded that the quaternary metal oxide films applied to Ti or Pt substrates exhibited high and persistent activity as anode materials for the electrochemical incineration of benzoquinone.

Feng et al. (2008) doped Gd into Ti-based Sb-SnO₂ anodes to investigate its performance on electrochemical destruction of phenol. They found that doping the anode with rare earth gadolinium (Gd) could improve the electrochemical oxidation rate of phenol. Cui et al. (2009a) prepared rare earth Ce, Eu, Gd and Dy doped Ti/Sb-SnO₂ electrodes by thermal decomposition and the performance of electrodes for the electro-catalytic decomposition of a model pollutant phenol was investigated. They also investigated the bisphenol A degradation on tin dioxide anode (Cui et al., 2009b).

Cossu et al. (1998) investigated landfill leachate oxidation on SnO₂ and PbO₂ anodes, respectively. Tin dioxide electrode showed similar performance as the PbO₂. Polcaro et al. (1999) studied electrochemical oxidation of 2-chlorophenol at Ti/PbO₂ and Ti/SnO₂ anodes. Results showed that, although similar average faradaic yields were obtained using Ti/PbO₂

or Ti/SnO₂ anodes, the latter material is preferred because of its better ability to oxidize toxic compounds.

Adams et al. (2009) fabricated four different SnO₂-based electrodes (SnO₂-Sb₂O₅/Ti, SnO₂-Sb₂O₅-PtO_x/Ti, SnO₂-Sb₂O₅-RuO₂/Ti and SnO₂-Sb₂O₅-IrO₂/Ti) using thermal decomposition method and systemically studied their stability and electrocatalytic activity towards the degradation of 2-nitrophenol (2-NPh), 3-nitrophenol (3-NPh) and 4-nitrophenol (4-NPh). It was found that by incorporating different metal oxides into the Sb-doped SnO₂ coating, the lifetime was significantly increased.

Wang et al. (2006) and Chen et al. (2010) found out that introducing trace amount of nickel into antimony doped tin oxide electrode could enhance its activity toward 4-chlorophenol and phenol degradation. The possible reason may be due to the hybrid effect of electro-oxidation and ozone oxidation because ozone could be in-situ generated on this type anode during electrolysis.

The doped tin dioxide electrode showed promising activity toward organics degradation, the activity in some cases is higher than lead dioxide, however its lifetime is shorter. Their stability must be improved further before its practical application in real wastewater treatment.

4. Diamond

Diamond is a fascinating material and exhibits many unique technologically important properties, including high thermal conductivity, wide band gap, high electron and hole mobility, high breakdown electric field, hardness, optical transparency and chemical inertness. Diamond has a cubic lattice constructed from sp³-hybridized tetrahedral arranged carbon atoms with each carbon atom bonded to four other carbon atoms. The stacking sequence is ABCABC with every third layer plane identical as showed in Fig. 7. This structure is fundamentally different from that of graphite. Impurities in diamond can make it an insulator with a resistivity of >10⁶ Ohm m and a band gap of 5.5 eV.

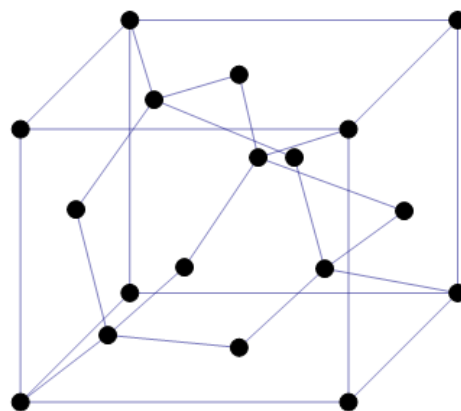


Fig. 7. Diamond lattice structure

4.1 Diamond preparation

Diamond films are usually synthesized by chemical vapor deposition (CVD). Early CVD of diamond was carried out by thermal decomposition of carbon containing gases under high

temperature. However, this technique may suffer low growth rate, which will retard its commercial application. In addition, the electrode may be contaminated with non-diamond carbon and required frequent interruptions to remove the accumulated graphite by hydrogen etching at high temperature.

In order to improve the diamond conductivity, boron was usually added to the diamond film as dopant. Boron to carbon ratio from ca. 0.02 to ca. 10^{-6} was widely accepted by different research groups. The standard method used for CVD boron doped diamond (BDD) was initially thermal diffusion and ion implantation (Prawer, 1995). These processes were made ex situ, after the film growth, and the no contamination of the growth reactor (Martin, et al., 1996.) is the main advantage. However, alternative techniques have shown that highly doped films could be prepared using in situ process from a solid source of boron inside the reactor and by introducing of B_2O_3 in a methanol-acetone mixture (Okano et al., 1990). It was observed better results evidenced by more homogeneity in films bulk, also showing a linear relation between the doping levels and boron concentration in the precursor source. Boron doping using other boron sources was also reported such as B_2H_6 by Mort et al. (1989) and Fujimori et al. (1990), while $B(OCH_3)_3$ was used as boron source by Ran et al. (1993).

4.2 Boron doped diamond (BDD) electrode application in waste water treatment

BDD film was found to be the most active anodic material for degradation of refractory or priority pollutants such as isopropanol and acetic acid (Foti et al., 1999), different carboxylic acids (Gandini et al., 2000), 4-chlorophenol (Rodrigo et al., 2001; Gherardini et al., 2001), phenol (Inieta et al., 2001b), 3-methylpyridine (Inieta et al., 2001a), benzoic acid (Montilla et al., 2002), polyacrylates (Bellagamba et al., 2002), 4-chlorophenoxyacetic acid (Boye et al., 2002) and an amaranth dyestuff (Hattori et al., 2003). All these investigations could confirm very high current efficiencies for COD removal, usually higher than 90%. Migliorinia et al. (2011) investigated the electrochemical degradation of Reactive Orange (RO) 16 Dye on BDD/Ti electrode.

BDD electrode as a developing anodic material showed very promising applications in electrochemical oxidation for waste water treatment due to its high energy efficiency and stability. However, its high cost and difficulty to find a proper substrate are its major drawbacks. In fact, only silicon, tantalum, niobium and tungsten as substrate can obtain stable diamond film. Silicon is brittle and its conductivity is poor. Tantalum, niobium and tungsten are too expensive. Titanium is a good candidate with low cost, strong mechanical strength and good electrical conductivity. However, diamond film deposited on titanium is not stable enough. During long term electrolysis, the diamond film can be detached from the titanium substrate. Thus there are still a lot of work to do before this promising anode material commercial available.

5. Other anodic materials

According to the model developed by Comninellis (1994), the Ta_2O_5 and Nb_2O_5 are also non-active anodes. Tantalum oxide and niobium oxide show very high electrochemical stability. They have powerful oxidizing ability and can be used to oxidize water to ozone efficiently (Santana et al., 2004; Da Silva et al., 2004; Kaneda et al., 2005; Awad et al. 2006; Kitsuka et al., 2007). Their preparation is usually followed a thermal decomposition method and the

procedure is similar to that of tin dioxide electrode except the coating solution used. Though they are non-active electrodes for oxygen evolution and may show high efficiency for toxic organics degradation, their application in waste water treatment is seldom reported except a few reports on ozone generation. Perhaps it is due to the high cost to prepare these types electrodes because precious metal is usually used.

6. Summary and prospect

In this section, the non-active anode materials including lead dioxide, tin dioxide, diamond, tantalum oxide and niobium oxide electrode were briefly reviewed from their fundamental concept, preparation techniques and application in waste water treatment by electrochemical oxidation. Electrochemical oxidation technology showed promising application in oxidation of toxic and non-biodegradable organic wastes. However, from the view point of anodic material, which is one of the key factors of the electrochemical oxidation system, there is still a lot of work to do before the electrochemical oxidation technology can be widely applied in real waste water treatment plants. For example, the cost of diamond shall be further decreased, while the stability of doped tin dioxide shall be improved.

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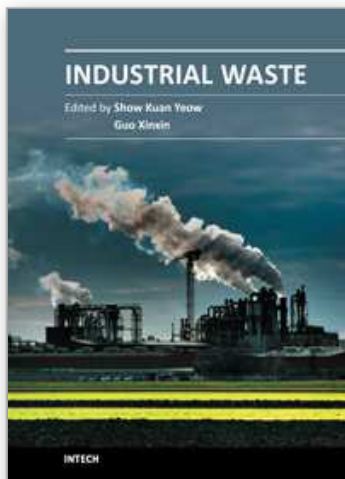
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This book is intended to fulfil the need for state-of-the-art development on the industrial wastes from different types of industries. Most of the chapters are based upon the ongoing research, how the different types of wastes are most efficiently treated and minimized, technologies of wastes control and abatement, and how they are released to the environment and their associated impact. A few chapters provide updated review summarizing the status and prospects of industrial waste problems from different perspectives. The book is comprehensive and not limited to a partial discussion of industrial waste, so the readers are acquainted with the latest information and development in the area, where different aspects are considered. The user can find both introductory material and more specific material based on interests and problems. For additional questions or comments, the users are encouraged to contact the authors.

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