

Chapter 2

Bibliography

2.1 Wastewater [5]

Water is a combination of two parts, hydrogen and oxygen as H_2O . However, pure water is only manufactured in a laboratory, water as we know, it is not pure hydrogen and oxygen. Even the distilled water we purchase in the store has measurable quantities of various substances in addition to hydrogen and oxygen. Rainwater, before it reaches the earth, contains many substances. These substances, since they are not found in pure water, may be considered as the impurities. When rain falls through the atmosphere, it gains nitrogen and other gases. As soon as the rain flows over land, it begins to dissolve from the earth and rocks such substances as calcium, magnesium, sodium, chloride, sulfate, iron, nitrogen, phosphorus, and many other materials. Organic matter is also dissolved by water from contact with decaying leaves, twigs, grass, or small insects and animals. Thus, a fresh flowing mountain stream may pick up many natural impurities, some possibly in harmful amounts, before it ever reaches civilization or is affected by the waste discharges of society. Many of these substances are needed in small amounts to support life and are useful to humans.

The waste discharge that first comes to mind in any discussion of stream pollution is the discharge of domestic wastewater, wastewater contains a large amount of organic waste. Industry also contributes

substantial amounts of organic waste. Some of these organic industrial wastes come from vegetable and fruit packing, dairy processing, meat packing, tanning and processing of poultry, oil, paper, and fiber (wood) and many more. All organic materials have one thing in common - they all contain carbon.

2.2 Restaurant wastewater [6]

Wastewater from restaurants and other commercial food service facilities differ significantly from residential wastewater. In addition to higher surge volumes during busy periods and generally higher temperature. The pollutants in restaurant wastewater are come from the cleaning of dishes, kitchen wares, meat and vegetable. Restaurant wastewater is typically higher in strength than residential wastewater. This due to the higher content in organic pollutants exactly oil and grease.

Oil and grease frequently cause problems of both wastewater collection and treatment systems. The problem occurs when oil and grease solidifies in sewage lines and will cover on the surface of treatment systems causing a decrease in the treatment system efficiency.

2.3 Wastewater treatment processes [7]

Wastewater treatment consists of applying known technology to improve or upgrade the quality of a wastewater. Usually wastewater

treatment will involve collecting the wastewater in a central, segregated location and subjecting the wastewater to various treatment processes. Most often, since large volumes of wastewater are involved, treatment processes are carried out on continuously flowing wastewaters or open systems rather than as batch or a series of periodic treatment processes in which treatment is carried out on parcels or batches of wastewaters. While most wastewater treatment processes are continuous flow, certain operations, such as vacuum filtration, involving as it does, storage of sludge, the addition of chemicals, filtration and removal or disposal of the treated sludge, are routinely handled as periodic batch operations. Wastewater treatment can be organized or categorized by the nature of the treatment process operation being used such as physical, chemical or biological treatment.

2.3.1 Physical treatment [7]

Sedimentation

Sedimentation is employed for the removal of suspended solids from wastewaters. The process can be considered in the three basic classifications, depending on the nature of the solids present in the suspension, there are discrete, flocculent and zone settling. In the discrete settling, the particle maintains its individuality and does not change in size, shape or density during the settling process. Flocculent settling occurs the particles agglomerate during the settling period with a resulting change in size and settling rate. Zone settling involves a flocculated suspension which forms a lattice structure and settles as a mass, exhibiting a distinct interface during the settling process. Compaction of the settled sludge occurs in all sedimentation but will be considered separately under thickening.

Flotation

Flotation is used for the removal of suspended solids, oil and grease from the wastewaters and for the separation and concentration of sludge. The waste flow of a portion of clarified effluent is pressurized to 3.4-4.8 atm in the presence of sufficient air to approach saturation. When this pressurized air-liquid mixture released to atmospheric pressure in the floatation unit, minute air bubbles are released from the solution. The sludge flocs, suspended solids or oil globules are floated by these minute air bubbles, which attach themselves to and became in the floc particles. The air-solids mixture rises to the surface, where it is skimmed off. The clarified liquid is removed from the bottom of the flotation unit, at this time a portion of the effluent may be recycled back to the pressure chamber. When flocculent sludges are to be clarified, pressurized recycle will usually yield a superior effluent quality since the flocs are not subjected to shearing stress through the pumps and pressurizing system.

Coagulation

Coagulation is employed for the removal of waste materials in suspended or colloidal form. Colloids are presented by particles over a range of 0.1-1.0 nm. These particles do not settle out on standing and cannot be removed by conventional physical treatment processes.

Colloids present in wastewater can be either hydrophobic or hydrophilic. The hydrophobic colloids possess no affinity for the liquid medium and lack stability in the presence of electrolytes. They are readily susceptible to coagulation. Hydrophilic colloids, such as proteins, exhibit a

marked affinity for water. The absorbed water retards flocculation and frequently requires special treatment to achieve effective coagulation.

Electrical properties of the colloids create a repelling force and prevent agglomeration and settling. Stabilizing ions are strongly adsorbed to an inner fixed layer which provides a particle charge that varies with the valence and number of adsorbed ions. Ions of an opposite charge form a diffuse outer layer which is held near the surface by electrostatic forces. The stability of a colloid is due to the repulsive electrostatic forces and in the case of hydrophilic colloids to solvation in which an envelope of water retards coagulation.

Adsorption

Many wastewaters contain organics which are refractory and which are difficult or impossible to remove by conventional biological treatment processes, such as acrylonitrile-butadiene-styrene (ABS) and some of heterocyclic organics. These materials can frequently be removed by adsorption on an active-solid surface. The most commonly used adsorbent is activated carbon. The solid surface in contact with the solution tends to accumulate a surface layer of solute molecules because of the unbalance of the surface forces. The physical adsorption results from molecular condensation in the capillaries of the solid. In general, substances of high molecular weight are most easily adsorbed. There is a rapid formation of an equilibrium interfacial concentration, followed by the slow diffusion into the carbon particles. The overall rate of adsorption is controlled by the rate of diffusion of the solute molecules within the capillary pores of the carbon particles. The rate varies reciprocally with the square of the particle diameter

and increases with the increasing of solute concentration and increasing of temperature, but decreases with the increasing of molecular weight of the solute.

2.3.2 Biological treatment [7]

The biological processes in treatment plants are carried out by a very diversified group of organisms. It is only possible roughly to list which species are present as it proves that the fauna in a treatment plant is very dependent on the external conditions.

All organisms in the biological treatment plant must necessarily have their origins from the outside; that is, they come from the wastewaters, from the air, the soil or from the animals which live close to the plant. An essential part of individual organisms has grown in the plant itself.

The two main types of biological treatment plants are activated sludge and biofilters treatment plants.

Activated sludge treatment

The principle in activated sludge treatment plants is that a mass of activated sludge is kept moving in the water by stirring or aeration. Apart from the living biomass, the suspended solids contain inorganic as well as organic particles. Some of the organic particles can be degraded by subjecting them to hydrolysis whereas others are non-degraded.

The amount of suspended solids in the treatment plant is granulated through the recycle of the suspended solids and by removing the so called-

excess sludge. The handling and disposal of the excess-sludge is one of the environmentally difficult problems in water treatment processes.

Biofilters

Biofilters are characterized by bacteria being attached to a solid surface in the form of a biofilm. Biofilm is a dense layer of bacteria characterized by their ability to adhere to a solid medium and form a fixed film of polymers in which the bacteria are protected against sloughing off. Biofilters have a short hydraulic retention time and hence free bacteria in the water will be washed out.

The disadvantage of the biofilters is the low efficiency of the biomass. The reason is that the substances must be carried through the biofilm to be removed by the bacteria. This transport takes place by molecular diffusion which is a slow process. In practice it proves that the general rule is that the removal is limited by diffusion. These phenomena must be understood in order to understand the functioning of biofilters.

2.3.3 Chemical treatment [7]

Ozonation

Ozone is a gas at normal temperature and pressure. As with oxygen, the solubility of ozone in water depends on temperature and the partial pressure of ozone in the gas phase and has recently been thought to also be a function of pH. Ozone is unstable and the rate of decomposition increases with temperature and pH. The decomposition is catalyzed by the hydroxyl radical (OH^\bullet), the radical decomposition product of ozone, the organic solute

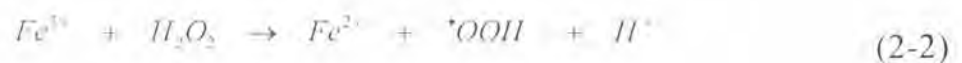
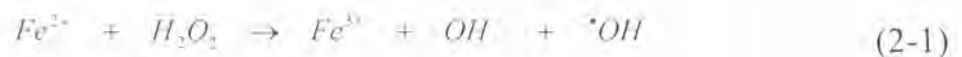
decomposition products and by variety of the other substances such as solid alkalis, transition metals, metal oxides and carbon. Under practical conditions, complete degradation of fairly unreactive compounds such as saturated hydrocarbons and halogenated aliphatic compounds does not occur with ozone alone, but current research has shown that ozone with addition of energy source such as sonification or ultraviolet readily decomposes these refractory compounds.

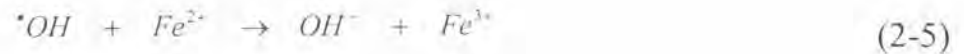
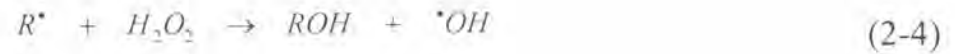
Ozonation of unsaturated aliphatic or aromatic compounds causes a reaction with water and oxygen to form acids, ketones and alcohols. At a pH greater than 9 in presence of redox salts such as Fe, Mn and Cu, aromatic may form some hydroxyaromatic structures (phenolic compound) with maybe toxic. Many of the byproducts of ozonation are readily biodegradable.

Organic removal is improved with the ultraviolet radiation. It is postulated that the ultraviolet activates the ozone molecule and may also activate the substrate. Ozone-ultraviolet is effective for the oxidative destruction of pesticides to terminal end products of CO₂ and H₂O.

Hydrogen peroxide

Hydrogen peroxide in the presence of a catalyst such as Iron, generated hydroxyl radical ([•]OH) which react with organics and reduced compounds in a similar to ozone [7].





Chlorine

Chlorine may be used as a chemical oxidant. In reaction with inorganic materials terminal end products usually result such as NaCl and nitrogen gas were produced from the oxidation of cyanide by using NaOCl as chlorine source. While chlorinated hydrocarbons were produced from organic oxidations.

Wet air oxidation

Wet air oxidation has been successfully applied in a number of applications for organics reduction. Wet air oxidation is based on a liquid phase reaction between organic materials in wastewater and oxygen supplied by compressed air. The reaction takes place flamelessly in an enclosed vessel, which is pressurized and at high temperatures, typically 136 atm gage and 288 °C. The system temperature is initiated by a startup boiler and maintained through autothermal combustion of organics once the reaction starts.

2.4 Electrochemical treatment [8]

Water treatment by electricity was used for several years, but electrochemical water or wastewater technologies did not find wide application by the limitation of relatively high capital investment and the expensive electricity supply. However, with the increasing standard of drinking water supply and the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the past two decades. There are companies supplying facilities for metal recoveries, for treating drinking water or process water, treating various wastewaters resulting from tannery, electroplating, dairy, textile processing, oil and oil-in-water emulsion, etc. Nowadays, electrochemical technologies have reached such a state that they are not only comparable with other technologies in terms of cost but also are more efficient and more compact. For some situations, electrochemical technologies may be the indispensable step in treating wastewaters containing refractory pollutants.

2.4.1 Electrocoagulation

Electrocoagulation involves the generation of coagulants in situ by dissolving electrically either aluminum or iron ions from aluminum or iron electrodes, respectively. The metal ions generation takes place at the anode, hydrogen gas is released from the cathode. The hydrogen gas would also help to float the flocculated particles out of the water. This process sometimes is called electroflocculation. It is schematically shown in Figure 2-1. The electrodes can be arranged in a mono-polar or bi-polar mode. The materials can be aluminum or iron in plate form or packed form of scraps

such as steel turnings, millings, etc. The chemical reactions taking place at the anode are given as follows.

For aluminum anode:



At alkaline conditions



At acidic conditions



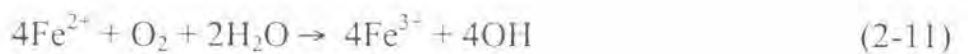
For iron anode:



At alkaline conditions



At acidic conditions



In addition, there is oxygen evolution reaction



The reaction at the cathode is

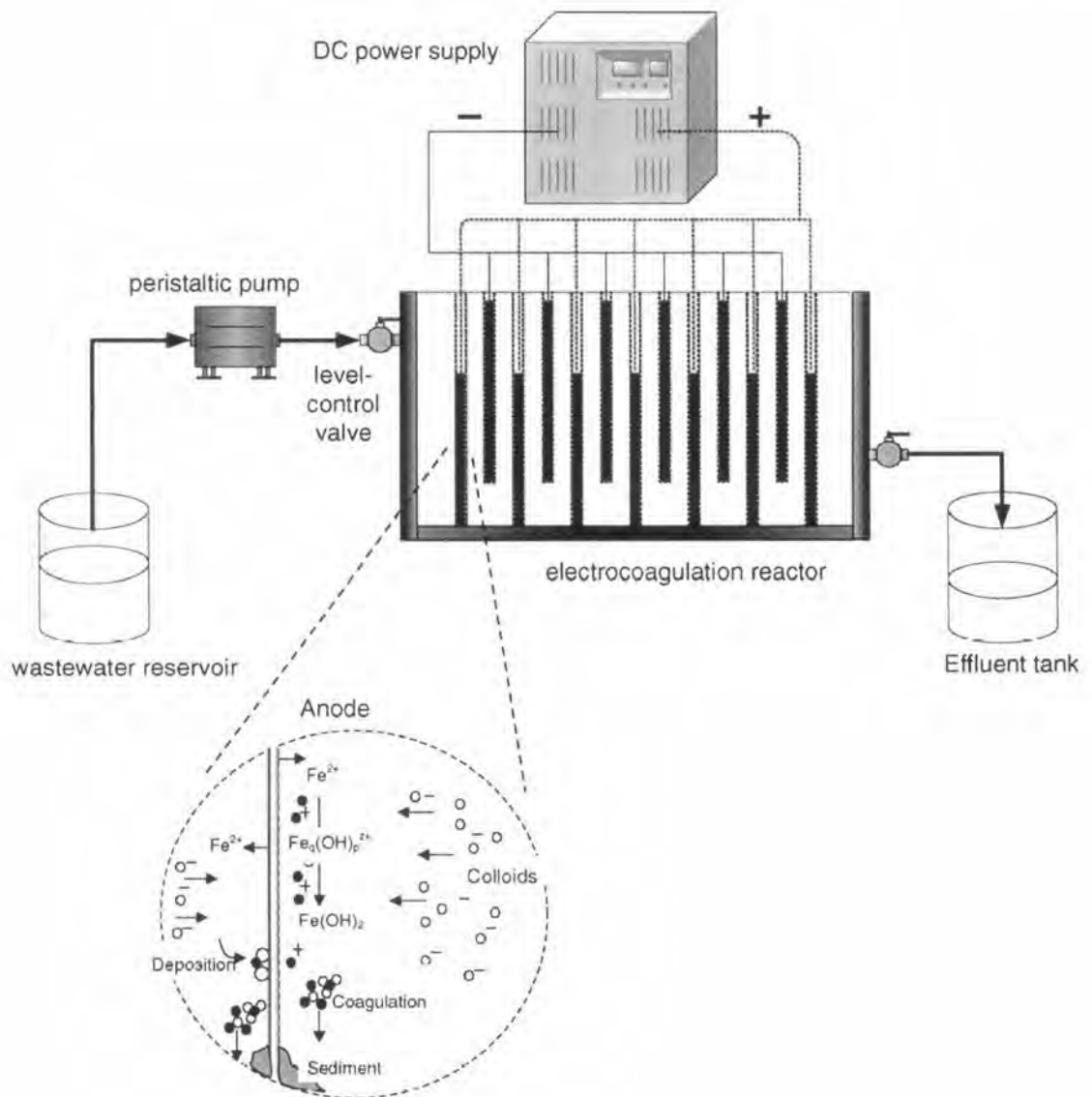


Figure 2-1 Schematic of electrocoagulation [9]

The Al^{3+} or Fe^{2+} ions are very efficient coagulants for particulates flocculating. The hydrolyzed aluminum ions can form large networks of Al-O-Al-OH that can chemically adsorb pollutants such as F^- . Aluminum is usually used for water treatment and iron for wastewater treatment [3]. The advantages of electrocoagulation include high particulate removal efficiency, compact treatment facility, relatively low cost and possibility of complete automation.

2.4.2 Electroflotation

Electroflotation is a simple process that floats pollutants to the surface of a water body by tiny bubbles of hydrogen and oxygen gases generated from water electrolysis. Therefore, the electrochemical reactions at the cathode and anode are hydrogen evolution and oxygen evolution reactions, respectively. Figure 2-2 represents the process of electroflotation.

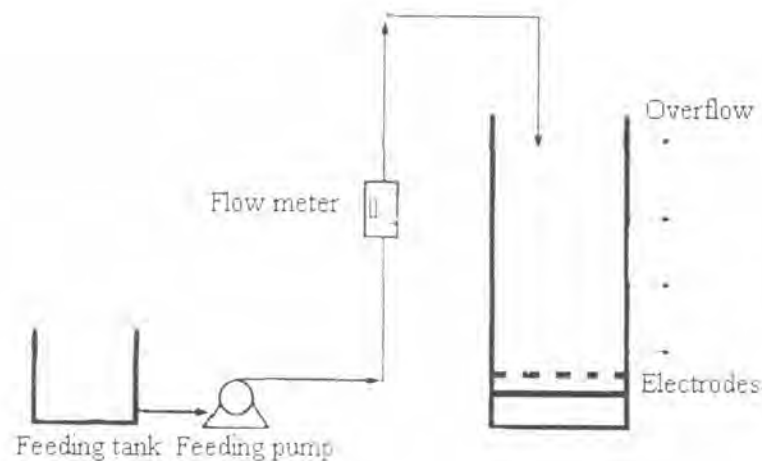


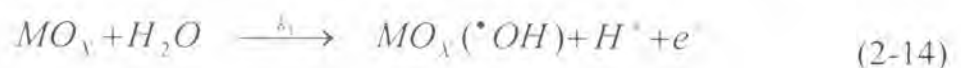
Figure 2-2 Electroflotation process [10]

2.4.3 Electrochemical oxidation

Study on electrochemical oxidation for wastewater treatment goes back to the 19th century, when electrochemical decomposition of cyanide was investigated [11]. Extensive investigation of this technology commenced since the late 1970s [8]. During the last two decades, research works have been focused on the efficiency in oxidizing various pollutants on different electrodes, improvement of the electrocatalytic activity and electrochemical stability of electrode materials, investigation of factors affecting the process performance, and exploration of the mechanisms and kinetics of pollutant degradation. Experimental investigations focus mostly on the behaviors of anodic materials, the effect of cathodic materials was not investigated extensively although Azzam et al. [12] have found a considerable influence of the counter electrode material in the anodic destruction of 4-chlorophenol.

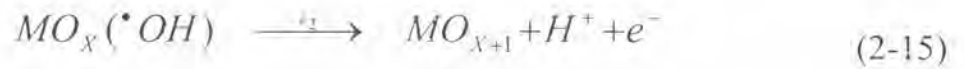
2.5 Mechanisms of electrochemical oxidation [7]

In Figure 2-3, a generalized scheme of the electrochemical conversion and combustion of organics on metal oxide anode (MO_x) is presented. In the first step, H_2O in acid or OH^- in alkali solution is discharged at the anode to produce adsorbed hydroxyl radical according to the equation (2-14).



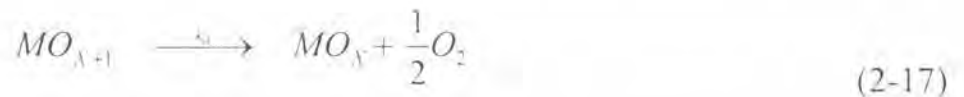
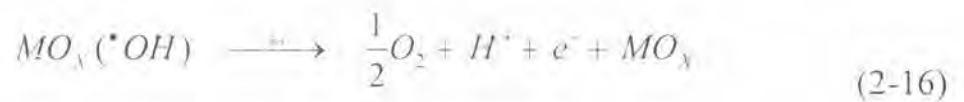
In the second step, the adsorbed hydroxyl radicals may interact with the oxygen already present in the metal oxide anode with possible transition

of oxygen from the adsorbed hydroxyl radical to the lattice of the metal oxide anode forming the so-called higher oxide (MO_{x+1}) as represented in equation (2-15).



Thus, we can consider that at the anode surface, two states of active oxygen can be presented in physisorbed active oxygen (adsorbed hydroxyl radicals, $\bullet OH$) and chemisorbed active oxygen (oxygen in the oxide lattice, MO_{x+1}).

In the absence of any oxidizable organics, the physisorbed and chemisorbed active oxygen produce dioxygen according to the equation (2-16) and (2-17).



Direct evidence for the last route of oxygen evolution at platinum oxide (PtO_x) is provided by the work of Rosenthal [13] who used ^{18}O as a tracer to show that portion of the evolved gas comes from oxygen already present in the oxide film. This view was put forward several times with other electrodes (RuO_2 , IrO_2 , $NiCo_2O_4$ and $NiOOH$) [14].

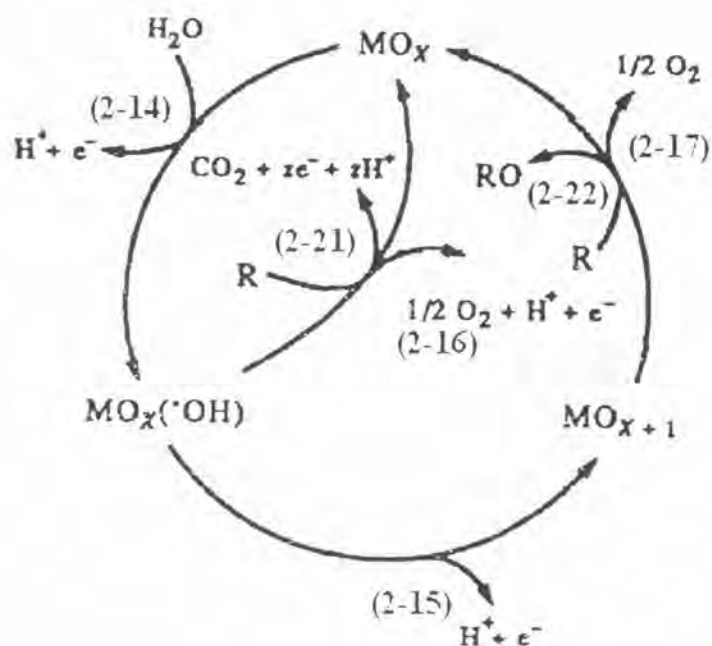
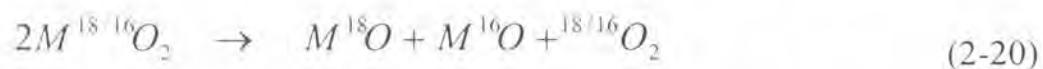
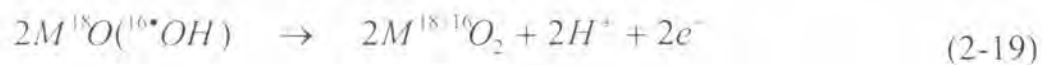
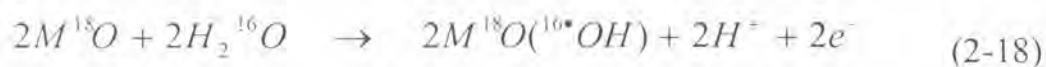


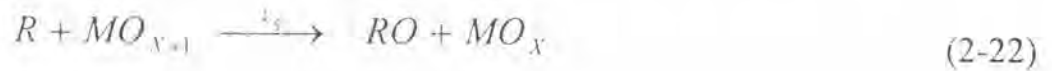
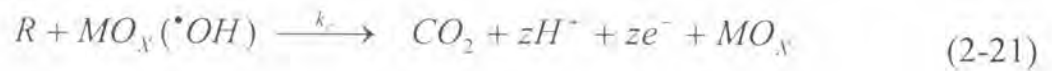
Figure 2-3 Generalized schema of the electrochemical conversion and combustion of organics with simultaneous oxygen evolution: (2-14) H_2O discharge and (2-15) transition of O from $'OH$ to the lattice of the oxide anode [7].

Such a result may be explained in terms of the equations (MO = oxide anode).



In the presence of oxidizable organics, it is speculated that the physisorbed active oxygen ($'OH$) should cause predominantly the complete

combustion of organics according to equation (2-21), and chemisorbed active oxygen (MO_{x+1}) participate in the formation of selective oxidation products as represented in equation (2-22).



2.5.1 Electrochemical conversion

For the electrochemical conversion of organics, the concentration of adsorbed hydroxyl radicals on the anode surface must be almost zero. To satisfy this condition, the rate of transition of oxygen into the oxide lattice in equation (2-15), must be much more faster than the rate of hydroxyl radicals formation in equation (2-14).

when

$$\text{Rate of hydroxyl radicals formation} = k_1[MO_x]$$

$$\text{Rate of transition of oxygen in the oxide lattice} = k_2[J]$$

$$k_2[J] \gg k_1[MO_x] \quad (2-23)$$

where

k_1 = Electrochemical rate constant for H₂O discharge

k_2 = Electrochemical rate constant for transition of
oxygen into oxide lattice

$[MO_x]$ = Concentration of active sites on the oxide anode

$[V]$ = Concentration of oxygen vacancies in the oxide
lattice.

Thus, efficient anodes for selective oxidation or electrochemical conversion of organics must have low concentration of active sites on the anode surface and must have a high concentration of oxygen vacancies in the oxide lattice.

Oxides forming is called higher oxide (MO_{x+1}) at potentials above the thermodynamic potential for O₂ evolution can be considered as oxides having a high concentration of oxygen vacancies and can favor selective oxidation of organics.

The current efficiency depends on the relative rate of the selective oxidation of organics, equation (2-22) to rate of oxygen evolution by decomposition of the higher oxide according to equation (2-17)

When

$$\text{Rate of selective oxidation of organics} = z_s k_s [O][R]_t$$

$$\text{Rate of } O_2 \text{ evolution by decomposition of } MO_{x-1} = k_d [O]$$

Where

z_s = Stoichiometry factor for selective oxidation;

k_s = Electrochemical rate constant for the selective oxidation of organics in equation (2-22)

k_d = Electrochemical rate constant for O_2 evolution in equation (2-17)

$[O]$ = Steady state concentration of active oxygen in the oxide lattice

$[R]_t$ = Concentration of organics at a given time, t

The instantaneous current efficiency (ICE) can be given by the relation in equation (2-24)

$$ICE = \frac{z_s k_s [R]_t}{z_s k_s [R]_t + k_d} \quad (2-24)$$

This relation shows that the instantaneous current efficiency for the selective oxidation is independent of the anode potential, but depends on the reactivity of organics. High ICE can be obtained with reactive organics and with anodes having low rate for the decomposition of their higher oxide.

2.5.2 Electrochemical combustion

For the combustion of organics, high concentration of hydroxyl radicals on the anode surface must be present. This is the case when the rate of hydroxyl radicals formation according to equation (2-14), is much faster than the rate of oxygen transition into oxide lattice as represented in equation (2-15). The following relation must be satisfied.

$$k_1[MO_x] \gg k_2[O_2] \quad (2-25)$$

Thus efficient oxide anodes for combustion of organics must have a large number of active sites for the adsorption of hydroxyl radicals and must have a very low concentration of oxygen vacancies in the oxide lattice.

Oxides in which the oxidation state of the cation is the highest possible and/or which contains an excess oxygen in the oxide lattice can be considered as oxides at the surface of which the hydroxyl radicals are accumulated and favor the combustion of organics.

The current efficiency for the combustion of organics depends on the relative rate of combustion of organics, represented in equation (2-21), to the rate of oxygen by discharge of the adsorbed hydroxyl radicals according to equation (2-16),

when

$$\text{Rate of combustion of organics} = z_c k_c [^*OH][R]_t$$

$$\text{Rate of O}_2 \text{ evolution by discharge of } ^*OH = k_0 [^*OH]$$

where

z_c = Stoichiometry factor for complete combustion of organics

k_c = Electrochemical rate constant for the combustion of organics

k_0 = Electrochemical rate constant for O₂ evolution

$[^*OH]$ = Steady-state concentration of adsorbed hydroxyl radicals at the oxide anode

$[R]_t$ = Concentration of organics at a given time

The instantaneous current efficiency for electrochemical combustion can be given by the relation.

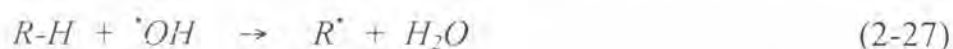
$$ICE = \frac{z_c k_c [R]_t}{z_c k_c [R]_t + k_0} \quad (2-26)$$

This relation shows that the instantaneous current efficiency for the combustion of organics depends on the nature of organics, its concentration, the anode material and on the anode potential. High instantaneous current

efficiency for the combustion of organics can be obtained with anodes having low electrochemical activity for O_2 evolution by discharge of hydroxyl radicals according to equation (2-16).

In the mechanism, it is very probable that dioxygen participates also in the combustion of organics according to the following reaction schema:

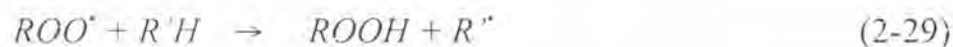
Formation of organic radicals by a hydrogen abstraction mechanism:



Reaction of the organic radicals with dioxygen formed at the anode:



Further abstraction of a hydrogen atom with the formation of an organic hydroperoxide (ROOH) and another organic radical:



Since the organic hydroperoxides formed are relatively unstable, decomposition of such intermediates often leads to molecular breakdown and formation of subsequent intermediates with lower carbon numbers. These scission reactions continue rapidly until the formation of carbon dioxide and water.

2.5.3 Electrochemical oxidation performance

There are several researchers' work on the parameters that affect on the electrochemical oxidation process efficiency. In this section, we literate on some important parameters for electrochemical treatment by electrochemical oxidation.

Support materials

Vercesi et al. [15] worked on searching for a good DSA-type O₂-evolving electrode based on the effects of support materials. Titanium, tantalum, zirconium, niobium and some of their alloys were used as support materials on the performance of IrO₂-Ta₂O₅ coated electrodes. The thermal behavior and oxygen affinity sequence of the metals, in relation to the electrode preparation procedure, were determined thermogravimetrically. The electrochemical corrosion of base metals was represented in Figure 2-4, the tantalum-based materials presented the highest stability with the minimum corrosion rate. The chemical and electrochemical stability of the base metals was found to be directly related to the service life of the electrode, measured in 30% H₂SO₄ at 80°C and 750 mA/cm². Tantalum-based electrodes represented the highest service life, 1700 h and 120 h for titanium-based electrodes.

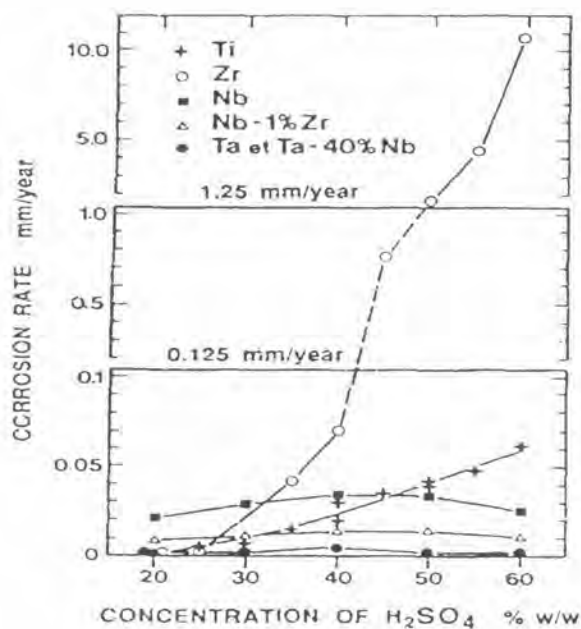


Figure 2-4 Electrochemical corrosion rate of base metals as a function of H₂SO₄ concentration at anode potential of 2 V/SCE

Coating materials

The active coating materials of electrodes are very important for pollutants degradation in electrochemical oxidation process. It could point the project to be benefit or insolvent. The coating enables the electrical charge transport between the base metal and the electrode/electrolyte interface. Its must have high chemical and electrochemical stability and able to catalyse the desired electrochemical reaction.

There is some works focus on the active coating materials for electrochemical degradation of organic pollutants presented in wastewater. Comninellis and Vercesi [16] found that the Ta₂O₅-doped IrO₂ represented

the highest service life. However, Comninellis [3] proposed in 1994 that the mechanism of electrochemical oxidation of organic pollutant on IrO_2 electrode was the electrochemical selective oxidation while that on SnO_2 electrode was the electrochemical combustion. On SnO_2 electrode, the organic pollutants were oxidized to CO_2 and water. Figure 2-5 represents the comparison of current efficiency of some various coating materials. The SnO_2 electrode presents the highest current efficiency. Because of its highest oxidation state which contains excess oxygen in the oxide lattice as possible. At SnO_2 surface, the hydroxyl radicals are accumulated and favor the combustion of organics while the other oxides having a high concentration of oxygen vacancies and can favor selective oxidation of organics more than combustion.

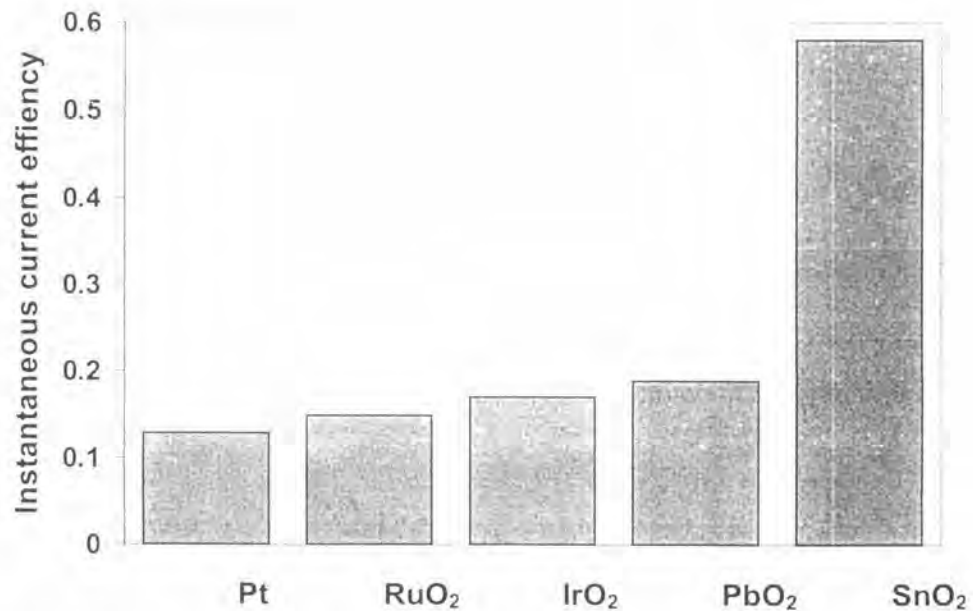


Figure 2-5 Instantaneous current efficiency of various coating materials [3, 16-17]

Not only SnO₂ electrode has the good attractive to be used as electrode for wastewater treatment in electrochemical oxidation, the diamond thin films have been widely used in electrochemical studies due to the unique properties like chemical stability, large potential range and mechanical resistance. Their applications embrace the electroanalysis, electrosynthesis, fuel cell and the organic pollutant degradation in wastewater [18]. Some studies showed that conducting diamond electrodes could be grown by energy-assisted (plasma or hot-filament) chemical vapor deposition on several substrates, such as silicon, titanium, niobium, tantalum, molybdenum, glassy carbon. Although all these substrates are currently used, they still have some drawbacks. In fact, a silicon substrate is very brittle. Nb, Ta, W are too expensive and the stability of the diamond layer deposited on the Ti substrate is still not satisfactory, because cracks may appear and cause the detachment of the diamond film during long-term electrolysis [19]. The organic compound electrochemical oxidation efficiency strongly depends on the used anode material and diamond is very interesting due to its superior properties [18]. In recent years, there are some publications on the application of diamond electrode for wastewater treatment [18-22]. However, the application of diamond electrode for organic pollutant degradation still limited due to the cost of diamond electrode is too expensive.

pH

Normally, the efficiency of the oxidation of organics tends to be superior in alkaline solution. That also holds for the anodic treatment using standard electrode materials. The wastewater accessible to treatment process has any pH and pH adjustment before treatment to the more favorable value

above 7 will be too expensive. Moreover, Stuki et. al. [23] proved that the degradation of benzoic acid was independent from pH on SnO₂ electrodes. Similar to Cañizares et. al [24] proposed that the pH does not influence in the global oxidation rate. It was higher initial oxidation rate in alkaline media. However, after the galvanostatic developed, the oxidation rate in acidic media surpasses those in the alkaline media. Because the accumulation of oxalic acid in alkaline media was higher than that in acidic media, due to its lower oxidizability at alkaline conditions.

Current density

The effect of current density was studied in many times, such as Comninellis and Nerini [17] in 1995, it was found that the degradation of phenol was independent from the current density. Figure 2-6 represents that the phenol elimination depends only on the specific electrical charge. Almost complete phenol elimination can be archived after the passage of an electrical charge 17-20 Ah/dm³.

The higher current densities increase the initial reaction rate (dCOD/dt) but decrease lightly the initial efficiencies of the process (dCOD/dQ). Nevertheless, both treatments end nearly at the same charge passed. This behavior is a characteristic of electrochemical systems in which both direct and mediated oxidation reactions play an important role. But the low current density experiment achieves initially a higher mineralization rate. This fact can be easily explained that the amount of oxalic acid accumulated in the high current density experiment is greater than those obtained in the low current density experiments [24].

Although, the current density might not affect on the kinetic of surface electrochemical oxidation of organic pollutant, but it also enhances the production of bulk chemicals, which may contribute, through parallel reaction schemes, to the degradation process.

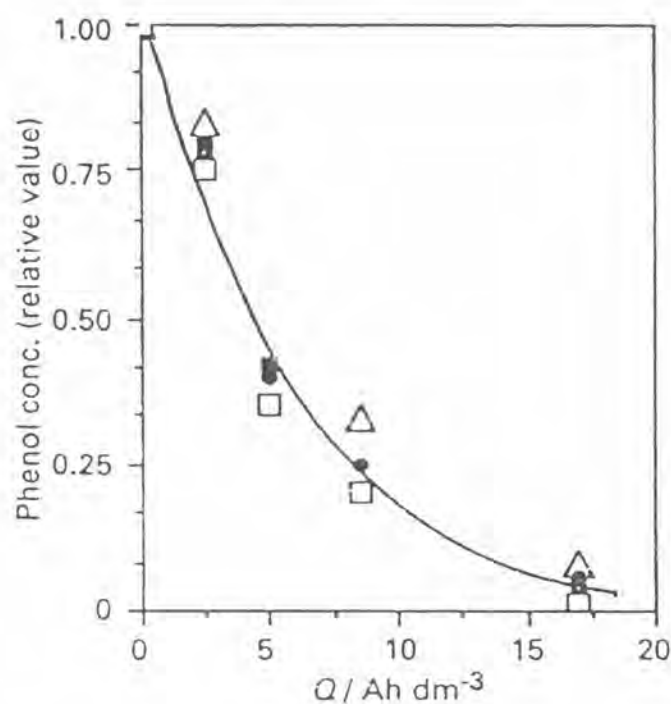


Figure 2-6 Influence of current density on the degradation rate of phenol, (Δ) 0.10 A/cm², (\bullet) 0.18 A/cm², (\square) 0.20 A/cm² and (\blacksquare) 0.30 A/cm² [17]

Temperature

An increase in the temperature leads to more efficient processes by global oxidation. While direct oxidation processes remain almost unaffected by temperature, this fact may be explained in terms of the presence of inorganic electrogenerated reagents. The oxidation carried out by these redox reagents is a chemical reaction. Consequently, its rate normally increases with temperature. But the oxidation process can be carried out either at the electrode surface and by electrogenerated reagents mainly hypochlorite and peroxodisulphates. However, the new organic intermediates are not formed with the increase of temperature, indicating that the process mechanisms do not vary with temperature [24].

2.6 Electrocatalytic electrodes [25]

Electrochemical degradation of organic pollutants which present in the wastewater needs the specific electrodes. The typical substrates are used as electrocatalytic electrodes must have the low voltage drop through the substrates and substrate-solvent interface. Many metallic electrodes could answer these criteria and many alloys can also be used as good composite electrodes covered with an active layer and for more long service life of electrodes.

The complexity of electrode behavior and our lack of detailed insight make it impossible to select the optimum electrode for a given process on a theoretical basis. Instead, an empirical approach must be used; the initial selection is based on process experience, and this is then tested and refined

during an extensive development program. Indeed, it is very difficult to predict the success of an electrode material or to define its lifetime without extended studies under realistic process conditions. Accelerated testing is rarely satisfactory except to indicate catastrophic failure.

There are some general guidelines to assist the choice of an electrode material;

Physical stability

The electrode material must have adequate mechanical strength, must not be prone to erosion by the electrolyte, reactants, or products, and must be resistant to cracking.

Chemical stability

The electrode material must be resistant to corrosion, unwanted oxide or hydride formation, and the deposition of inhibiting organic films under all conditions (e.g., potential and temperature) experienced by the electrode.

Suitable physical form

It must be possible to fabricate the material into the form demanded by the reactor design, to facilitate sound electrical connections, and to permit easy installation and replacement at a variety of scales. The shape and design of the electrode may take into account the separation of products, including the disengagement of gases or solids.

Rate and product selectivity

The electrode material must support the desired reaction and, in some cases, significant electrocatalytic properties are essential. The electrode material must promote the desired chemical change while inhibiting all competing chemical changes.

Electrical conductivity

This must be reasonably high throughout the electrode system including the current feeder, electrode connections, and the entire electrode surface exposed to the electrolyte. Only in this fashion it is possible to obtain a uniform current and potential distribution as well as to avoid voltage losses leading to energy inefficiencies.

Cost/lifetime

A reasonable and reproducible performance including a lifetime probably extending over several years must be achieved for an acceptable initial investment.

It is important to note that the choice of working and counter electrodes cannot be made independently since the chemistry at each has consequences to the solution composition throughout the cell. Indeed, the selection of electrode material and its form must be an integrated decision within the prospective of the cell and process design. In some cases such as the manufacture of pharmaceutical products, the electrodes and their compounds must have a low toxicity.

2.7 The influence of electrode material on process performance

[25]

This section is literated the ways in which the choice of electrode material influences the design of electrochemical reactors and process performance.

Energy Consumption

The specific energy consumption should be minimized in order to minimize the power costs. In general, the total power requirement has contributions for both electrolysis and movement of either the solution or the electrode. The design of electrodes and cell has an important role in reducing each of these components. Thus, a very open flow-through porous electrode will have a low pressure drop associated with it, giving rise to modest pumping costs and facilitating reactor sealing. A high surface area electrode which itself a turbulence promoter in bed electrode, will give rise to a moderately high mass transfer coefficient and active area without the need for high flow rates through the cell; the pumping cost will again be moderately low.

The direct electrolytic power could be minimized by

- Obtaining a current efficiency approaching 1.0
- Minimizing the cell voltage.

It is therefore important to select the electrode material and operating conditions so as to maintain a high current efficiency. This also assists the

operation of the process by reducing the amount of product purification that is necessary and/or byproducts that must be handled.

The cell voltage is a function of the reversible cell voltage, the over-potentials at the two electrodes, and ohmic drops in the electrolyte, the electrodes, busbars etc., and any separator in the cell. Again, the maintenance of a low cell voltage demands attention to the design of both electrodes and cell. Where possible, the following features should be included:

- The counter electrode reaction should be chosen so as to minimize the reversible cell voltage. This requires the availability of a suitably stable electrode material.
- The over-potentials at both electrodes should be minimized by the use of electrocatalysts.
- The electrodes, current feeders, and connectors should be made from highly conducting materials to lower ohmic drops.
- The electrodes should facilitate low IR drop in the electrolyte by, for example, allowing efficient gas disengagement and passage out of the interelectrode gap. Meshes as well as louvred and lantern blade electrodes can be used.
- Electrode and cell design should allow a small interelectrode or electrode membrane gap. In the limit the electrode may touch the membrane as in zero-gap or solid polymer electrolyte cells.
- A separator should be avoided by suitable selection of the counter electrode chemistry or, if essential, a thin conductive membrane should be used.

Current efficiency

Current efficiency is the fraction of the total charge passed that is used in the formation of the desired product. This can be a strong function of electrode material, e.g., because of differences in the rate of hydrogen evolution as a competing reaction. Competing reactions can also lead to the corrosion and/or erosion of the electrode material as well changes to the electrode (e.g., by formation of a hydroxide or oxide or the deposition of another metal onto the surface).

Material Yield

This is the fraction of the starting material that is converted into the desired product. This is also dependent on electrode material in many cases. Values less than one indicate byproducts and hence perhaps the need to introduce additional purification steps that inevitably increases the complexity of the overall process and costs.

Space-Time Yield

One of the most valuable statements of reactor performance is the space-time yield or weight of product per unit time per unit volume of reactor. It is determined by the current density, the current efficiency, and the area of electrode per unit volume of cell, all dependent on the electrode material and its form. Commonly, the cell is operated in conditions where the electrode reaction is mass transport controlled (especially when a high fractional conversion is desirable or when the concentration of reactant is limited by solubility or process considerations. Then the current density is determined by the concentration of reactant and the mass transport condition.

The latter is therefore frequently enhanced by the use of high flow rates, turbulence promoters, and/or electrode movement.

The current is proportional to the active electrode area in the cell. A compact cell design requires a high area per unit cell volume. This suggests the use of a three-dimensional electrode but such electrodes make it difficult to maintain a uniform fluid flow and electrode potential, i.e., to control the reaction environment. Hence, the use of porous, flow-through electrodes often involves a trade-off between enhanced electrode area and material yield and/or current efficiency.

Ease of product isolation

Many industrial electrosyntheses benefit from clever process design to reduce the number of steps in the product isolation and purification. This can be critical to the process economics.

Other Factors

Of course, other factors are important in the design of electrodes and cells. These include cost, safety, ease of maintenance, and convenience to use. It is also essential that the performance of the electrodes is maintained throughout the projected operating life of the cell, maybe several years. Examples of problems that frequently arise include (a) deposition onto cathode surfaces of hydrogen evolution catalysts due to trace transitional metal ions in the electrolyte and (b) poisoning of PbO_2 anodes by organic molecules leading to enhanced corrosion as well as oxygen evolution.

2.8 SnO₂ type dimensionally stable anodes (DSA)

The discovery of the dimensionally stable anodes (DSA) has brought significant improvements in the chlor-alkali industry and in many other applications such as water electrolysis, metal electrowinning, selective synthesis and destructive oxidation of organic contaminants [26]. The DSA electrodes consist of a pure or mixed metal oxide coatings deposited on a base metal using an appropriate precursor.

The pure SnO₂ is an n-type semiconductor with a direct band gap of roughly 3.5 eV and can be used as an electrode material with reasonable conductivity only at high temperatures. The doped SnO₂ has been used as transparent electrode material in photoelectrochemistry. The electrochemical properties of polycrystalline as well as single crystalline, SnO₂ were investigated by several researchers [27].

The combination of high chemical and electrochemical stability as a consequence of the rather large band gap, high conductivity of doped SnO₂ and the high oxygen evolution overpotential, makes SnO₂ an attractive electrode material for the anodic oxidation of organics in aqueous solutions [27]. The crystalline structure of SnO₂ is presented in Figure 2-7 [28].

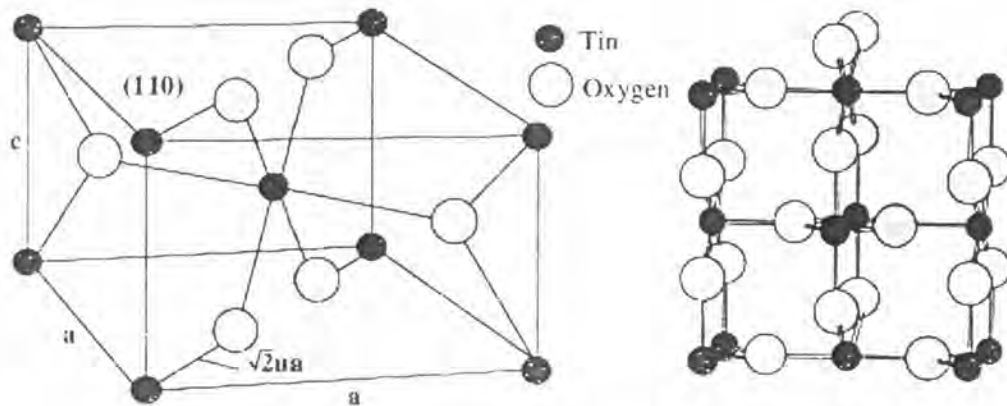


Figure 2-7 The crystalline structure of SnO₂ [28]

2.8.1 Preparation of SnO₂ type dimensionally stable anodes

There are a variety of methods available for coating the catalyst support for obtains the dimensionally stable anodes;

Sputtering [29]

The principle of sputtering is relatively simple. A source, also called the target is bombarded in a high vacuum with gas ions that have been accelerated by a high voltage, producing a glow discharge or plasma. Atoms from the target are ejected by momentum transfer and move across the vacuum chamber to be deposited on the substrate to be coated.

Very low initial pressure is required to remove impurities from the system. The development of a magnetically enhanced cathode or magnetron has considerably expanded the potential of sputtering. The magnetron sends

the electron into spiral paths to increase collision frequency and enhance ionization.

Reactive sputtering occurs when the species are sputtered in a reactive atmosphere such as nitrogen or methane. The process is now used extensively for the deposition of nitrides and carbides. Sputtering can produce a wide variety of coatings with excellent adhesion and good composition control, without the high temperature requirements as CVD. Its major disadvantages are its low deposition rate and its line-of-sight characteristic. The latter can be overcome to some extent by operating at higher pressure, but at some sacrifice in deposition rate.

Ruske et. al. [30] studied the coating of SnO_2 on silicon wafer by DC and MF reactive sputtering in Ar/O_2 atmosphere with the system was represented in Figure 2-8. The higher film densities and hardness were observed for MF sputtering coating. The morphology of samples coated by MF sputtering were strongly depend on deposition pressure, it was changed from close-packed fibrous grains to columnar structure when deposition pressures increased from 0.3 to 1.0 Pa. The crystal orientation of DC sputtering films changed from 110 to 101 with the increasing of 0.3 to 0.6 Pa. It also changed from 110 to 211 for MF coated films with the increasing of deposition pressure from 0.3 to 1.0 Pa. The internal stress is higher for MF coated film. However, it could be reduced by increasing of deposition pressure.

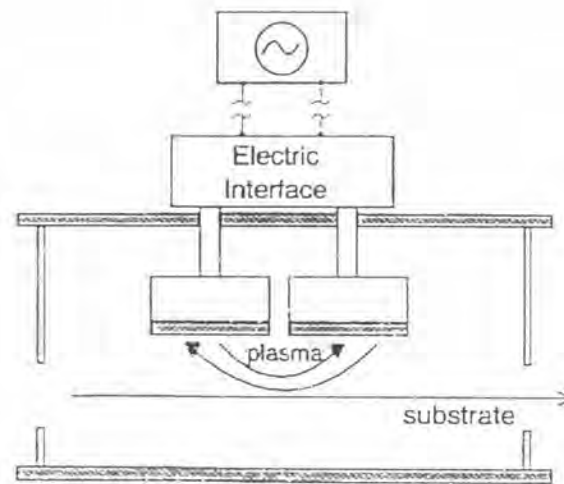


Figure 2-8 Schematic overview of a medium frequency (MF) powered twin magnetron reactive sputtering system [30]

Sol-gel dip coating [29]

Sol-gel processing or, more broadly speaking, the processing of ceramics and glasses from chemical precursors, is an emerging technology with a great potential especially in coatings and fiber production. At present, the development of sol-gel is still predominantly in the laboratory, yet it has spurred a great deal of interest in high-technology industries such as semiconductors, optoelectronics, optics, and structural ceramics. Sol-gel is already used in a sizable range of applications particularly in thin films. These applications include the spin-on-glass (SOG) process which is used in semiconductor fabrication and the coating of architectural glass to control optical properties.

The sol-gel process uses a liquid reactive precursor material that is converted into the final product by chemical and thermal means. This precursor is prepared to form a colloidal suspension or solution (sol) which goes through a gelling stage (gel) followed by drying and consolidation. The process requires only moderate temperatures, in many cases less than half the conventional glass or ceramics processing temperatures. It also permits very close control of the composition and structure of the deposit on the molecular level and makes possible the production of near-net shapes. These are very important advantages.

A number of processing problems still need to be solved. The need for better control of shrinkage and cracking is critical. The cracking of coating was presented in Figure 2-9 [31]. Moreover, the cost of precursor materials is still high, although it is likely to come down as applications are developed and consumption increases.

Liu et. al. [32] prepared the $\text{IrO}_2/\text{SnO}_2$ mixed oxide electrodes by sol-gel technique. The prepared electrodes were prepared by brushed precursor solution on titanium substrates and annealed at various temperatures. It was found that the crystalline IrO_2 and SnO_2 were formed at 300 °C or higher. However, the best annealing temperature was 400 °C.

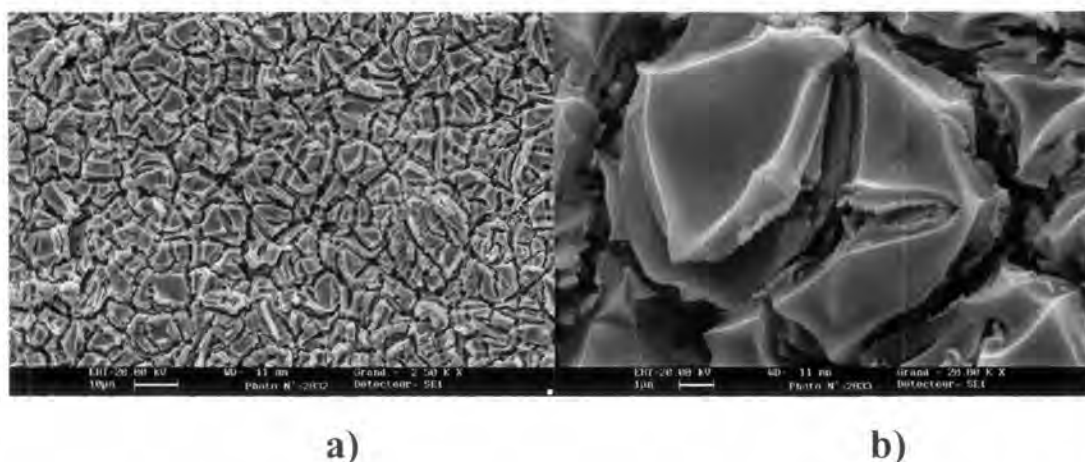


Figure 2-9 Cracking of IrO₂ layer by sol-gel dip coating technique a) 2,500X and b) 20,000X [31]

Spray pyrolysis [33]

In the spray deposition process, a precursor solution is pulverized by means of a neutral gas, so that it arrives at the substrate in the form of very fine droplets. The constituents react to form a chemical compound onto the substrate. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition.

Figure 2-10 represents a typical spraying system [33]. It mainly consists of spray nozzle, precursor solution, substrate heater, temperature controller and air compressor or gas propellant. To measure flow of precursor solution and air, liquid and gas flow meters are used. Vertical and slanted spray deposition arrangements with stationary or linearly moving spray nozzle are frequently used in this technique. To achieve uniform deposition the moving arrangements (either nozzle or substrates or both)

have been used. Sometimes the spray assembly is mounted on a moving table and is rastered across the substrates using stepping motors.

The properties of the film depend upon the anion to cation ratio, spray rate, substrate temperature, ambient atmosphere, carrier gas, droplet size and also the cooling rate after deposition. The film thickness depends upon the distance between the spray nozzle and substrate, substrate temperature, the concentration of the precursor solution and the quantity of the precursor solution sprayed.

The film formation depends on the process of droplet landing, reaction and solvent evaporation, which are related to droplet size and momentum. An ideal deposition condition is when the droplet approaches the substrate just as the solvent is completely removed. Lampkin [34] showed that, depending on droplet velocity and flow direction, a droplet will flatten, skip along the surface or hover motionless.

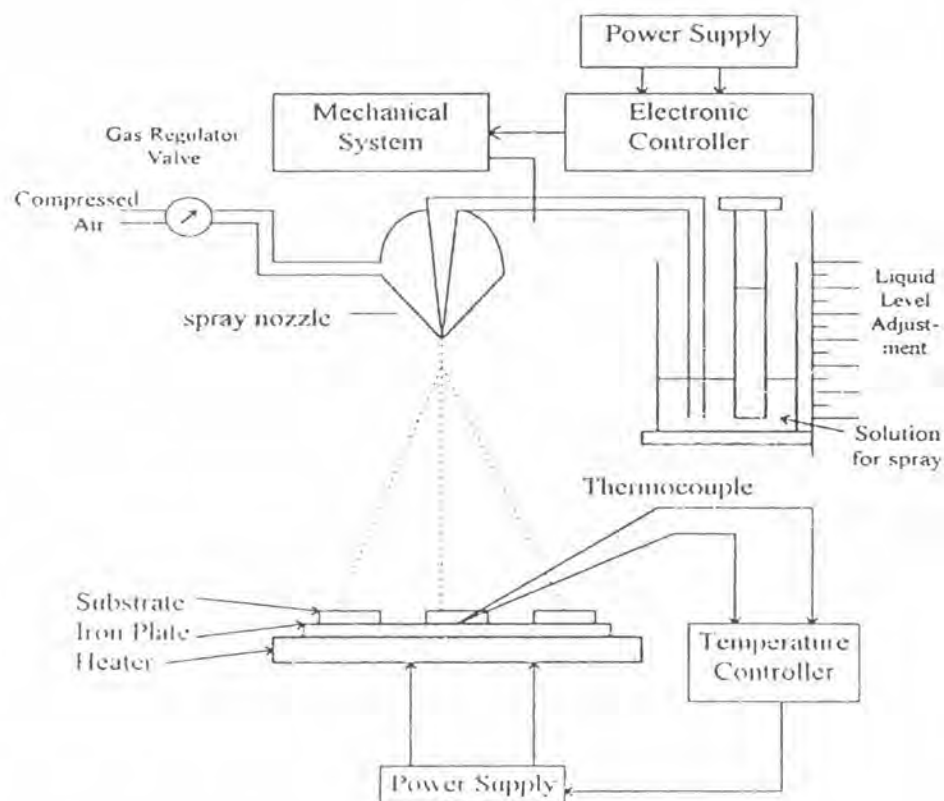


Figure 2-10 Schematic set-up for spray pyrolysis technique [33]

Kötz et. al. [27] prepared the Sb, F and Cl doped SnO_2 electrodes on titanium substrate by using of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ as precursor and SbCl_3 , NH_4F and residue Cl were used as doping agent at temperature around 500°C . The best composition of spray solution was found to be 10 g of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ and 0.1 g of SbCl_3 in 100 ml of ethanol. The results represented that lowest resistance films are fluorine doped SnO_2 film at temperature between $400\text{--}500^\circ\text{C}$. At reference current density 0.1 mA/cm^2 in $0.1\text{ N H}_2\text{SO}_4$ the oxygen evolution potential increased for 1.50 to 1.65 and to 1.95 V/SCE for Pt, PbO_2 and prepared SnO_2 electrode, respectively. Furthermore, it was found that the reaction mechanism of phenol anodic oxidation on SnO_2 electrode was different from that on Pt/Ti electrode. The quinone intermediates was not formed in the reaction. That means that either the quinones are much more

rapid oxidized on SnO_2 than on platinum or the ring-opening of phenol was occurred as the first step of the reaction.

2.9 Chemical vapor deposition [35]

Chemical vapor deposition (CVD) is the process of chemically reacting a volatile compound of a material with other gases to be deposited, to produce a nonvolatile solid that deposits atomistically on a suitably placed substrate. It differs from physical vapor deposition (PVD), which relies on material transfer from condensed-phase evaporant or sputter target sources. Because CVD processes do not require vacuum or unusual levels of electric power, they were practiced commercially prior to PVD. A century ago, CVD methods were used to deposit a protective tungsten coating on carbon filaments in an attempt to extend the life of incandescent lamps. Today, high-temperature CVD processes for producing thin films and coatings have found increasing applications in such diverse technologies as the fabrication of solid-state electronic devices, the manufacture of ball bearings and cutting tools, and the production of rocket engine and nuclear reactor components. In particular, the need for high-quality epitaxial films with single crystal in both silicon and compound-semiconductor technology, coupled with the necessity to deposit associated insulating and passivating films, has served as a powerful driver spurring the development of CVD processing methods.

Among the reasons for the growing adoption of CVD methods is the ability to produce a large variety of films and coatings of metals, semiconductors and inorganic as well as organic compounds in either a

crystalline or vitreous form, possessing desirable properties. Furthermore, the ability to controllably create films of widely varying stoichiometry makes CVD unique among deposition techniques. Other advantages include the affordable cost of the equipment and operating expenses, the suitability for both batch and semi-continuous operation, and the compatibility with other processing steps. Because of this, many variants of CVD processing have been researched and developed, including atmospheric pressure (APCVD), low-pressure (LPCVD), plasma-enhanced (PECVD), and laser-enhanced (LECVD) chemical vapor deposition. Hybrid processes combining features of both physical and chemical vapor deposition have also emerged.

The fundamental sequential steps that occur in every CVD process are sketched in Figure 2-11. and include:

1. Convective and diffusive transport of reactants from the gas inlets to the reaction zone
2. Chemical reactions in the gas phase to produce new reactive species and by-products
3. Transport of the initial reactants and their products to the substrate surface
4. Adsorption (chemical and physical) and diffusion of these species on the substrate surface
5. Heterogeneous reactions catalyzed by the surface leading to film formation
6. Desorption of the volatile by-products of surface reactions
7. Convective and diffusive transport of the reaction by-products away from the reaction zone

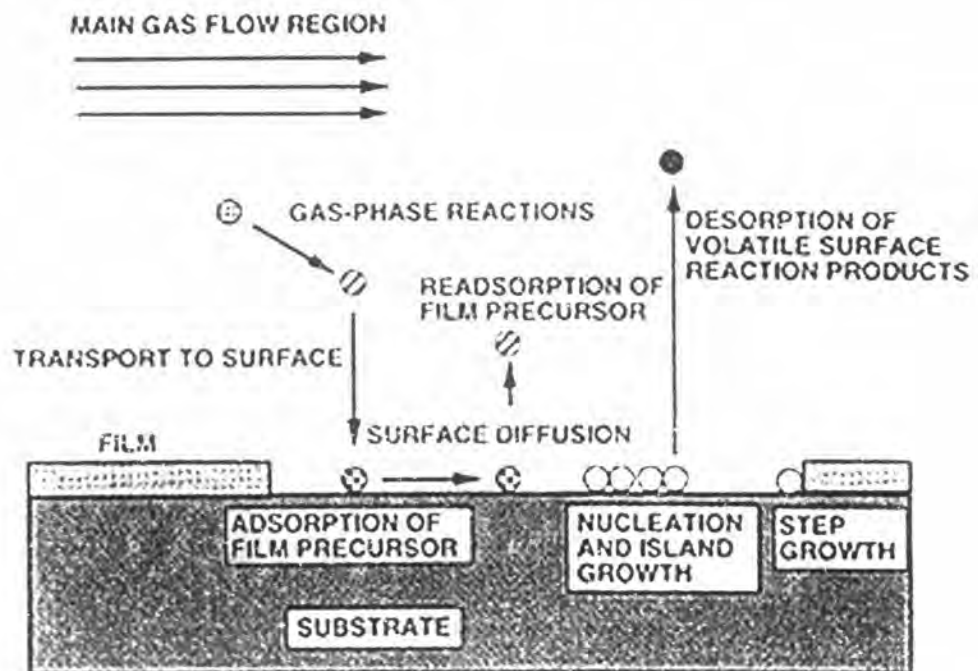


Figure 2-11 Sequence of gas transport and reaction processes contributing to CVD film growth [35]

Figure 2-12 provides a perspective that integrates many of these steps, here subdivided into coordinates related to basic chemistry and physics, gas transport phenomena and to the reactors that must efficiently deposit films.

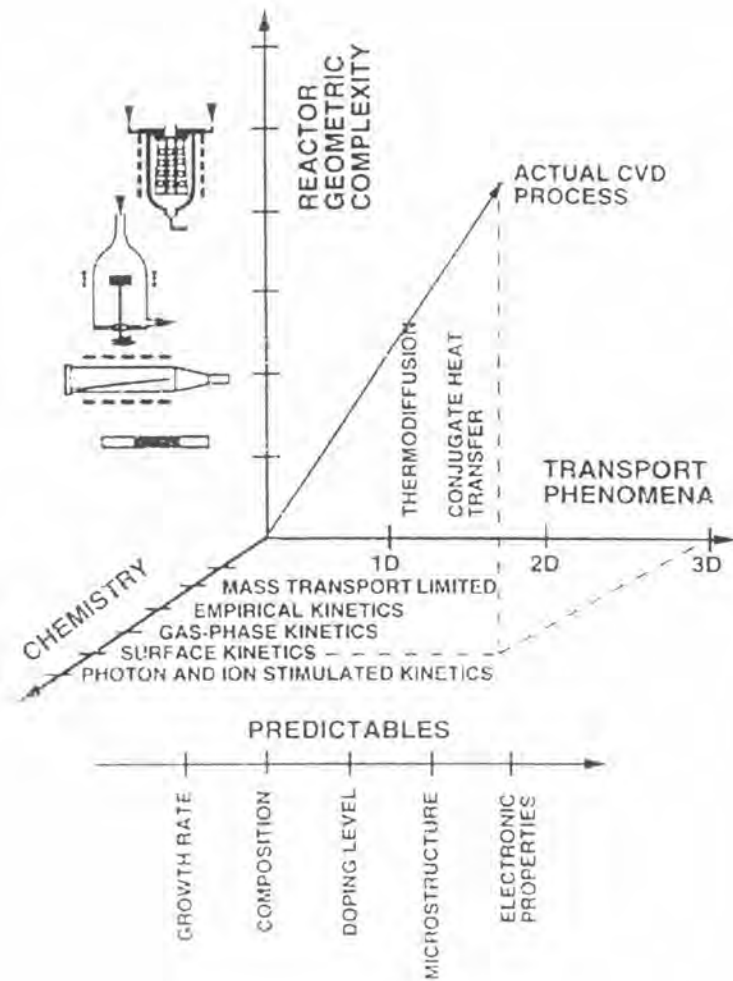


Figure 2-12 Schematic diagram of chemical, transport and geometrical complexities involved in modeling CVD process [35]

2.9.1 Thermodynamics of chemical vapor deposition [35]

Reaction feasibility

Thermodynamics addresses a number of important issues with respect to CVD. Once it is decided that a reaction is possible, thermodynamic

calculation can frequently provide information on the partial pressures of the involved gaseous species and the direction of transport in the case of reversible reactions. Importantly, it provides an upper limit of what to expect under specified conditions. However, address questions related to the speed of the reaction and resulting film growth rates. Actually, processes which are thermodynamically possible frequently proceed at such low rates because of both vapor transport kinetics and vapor-solid reaction limitations that they are unfeasible in practice. Furthermore, the use of thermodynamics implies that chemical equilibrium has been attained. Although this may occur in a closed system, it is generally not the case in an open or flow reactor where gaseous reactants and products are continuously introduced and removed. In general, CVD may be viewed as an empirical science with thermodynamic guidelines.

Condition of equilibrium

Thermodynamics can provide us with much more than a prediction of whether a reaction will proceed or not. Under certain circumstances, it can yield quantitative information on the operating intensive variables which characterize the equilibrium. The problem is to evaluate the partial pressures or concentrations of the involved species within the reactor given the reactant compositions and operating temperature. In practice, the calculation is frequently more complicated than initially envisioned because in situ mass spectroscopic analysis of operating reactors has surprisingly revealed the presence of unexpected species which must be accounted.

2.9.2 Thermal chemical vapor deposition processes [35]

This topic builds on the fundamentals of gas flow and reactions in CVD processes by describing their practical exploitation in producing films and coatings of interest. Most CVD processes can be conveniently subdivided into two categories. Thermal CVD processes employ heat energy to activate the required gas and gas-solid phase reactions. In contrast, the plasma-enhanced CVD processes derive benefit from plasma activation of the involved chemical species. However, even with similar input gases used to deposit the same nominal materials, films produced by thermal and plasma CVD processes can differ widely with respect to film structure, composition, and properties.

The great variety of materials deposited by thermal CVD methods has inspired the design and construction of an equally large number of processes and systems. Thermal processes have been broadly differentiated by such descriptors as low and high temperature, atmospheric and low pressure, cold and hot wall, and closed and open system. Within a specific category of process, the variations in design and operating variables frequently make it difficult to compare performance of individual systems or reactors, even when depositing the same material. Regardless of process type, however, the associated equipment must have the following capabilities:

1. Deliver and meter the reactant and diluent gaseous into the reactor
2. Supply heat to the substrates so that reaction and deposition can proceed efficiently
3. Remove the by-product and depleted gases

2.9.3 Metal-organic chemical vapor deposition (MOCVD)

Metal-organic chemical vapor deposition is sometime called organometallic vapor phase epitaxy (OMVPE) or metal-organic vapor phase epitaxy (MOVPE) [36]. It was originally developed in the late 1960s to grow epitaxial compound semiconductor films [37]. Metal-organic chemical vapor deposition is a specialized area of chemical vapor deposition which utilizes metal-organic compounds as precursors usually in combination with hydrides or other reactants [29]. The early results demonstrated that deposition of critical semiconductor materials could be obtained at lower temperature than conventional thermal CVD in a continuous flow process and that epitaxial growth could be successfully achieved. The quality of the equipment and the diversity and purity of the precursor chemicals have steadily improved since then and the process is being refined constantly [38].

A wide variety of materials can be deposited by MOCVD, either as single crystal, polycrystalline or amorphous films [39]. The most important application is deposition of the group III-V semiconductor compounds [29].

Metal-organic chemical vapor deposition possess has the high potential for large-area deposition, good composition control and film uniformity, high film-deposition rates and densities, and conformal step coverage. The success of MOCVD strongly hinges on the availability of suitable precursors [35].

The great advantage of metal-organics is their generally high volatility at moderately low temperatures. Since all constituents are in the vapor phase, precise electronic control of gas flow rates and partial pressures is possible

without dealing with troublesome liquid or solid sources in the reactor. That, combined with pyrolysis reactions which are relatively insensitive to temperature, allows for efficient and reproducible deposition. Carbon contamination of films is a disadvantage of MOCVD [35], but it was solved by the addition of co-reagent in the gas phase to eliminate the carbon impurity [4].

The commercial scale-up of metal-organic chemical vapor deposition requires the following:

1. Batch precursor amounts must rise from a few grams to a few kilograms
2. Production yields must rise and quality be consistent
3. The environmental impact must be minimal
4. Safety must be assured

2.9.4 Metal-organic chemical vapor deposition of tin oxide (SnO₂)

For SnO₂, there are several researchers have studied about the preparation of SnO₂ thin films by metal-organic chemical vapor deposition and some parameter effects on coating performance and film properties were studied [40-43].

There is some organo-tin which can be used as precursors for preparation of SnO₂ in MOCVD process. Table 2-1 represents some information about various organo-tin precursors.

Kaminori and Mizuhashi [42] studied MOCVD of SnO₂ by various organo-tin, dibutyl tin diacetate (DTD), tetrabutyl tin (TBT), tetraethyl tin (TET) and tetramethyl tin (TMT) were used in their work. The depositions were performed in the cold-wall CVD reactor with rotating substrate holder. They found that, the best tin precursor is TET because of its molecular size is most appropriate for forming of regularly arranged Sn-O bonds leading to the prepared SnO₂ film with good crystallinity.

Table 2-1 represents properties of various organo-tin

Precursor name	Molecular formula	Melting point (°C)	Boiling point (°C)
Dibutyl tin diacetate ¹	(C ₄ H ₉) ₂ Sn(CH ₃ COO) ₂	12	>200
Tetrabutyl tin	Sn(C ₄ H ₉) ₄	-97	127-145 ²
Tetraethyl tin	Sn(C ₂ H ₅) ₄	-112	181 ³
Tetramethyl tin	Sn(CH ₃) ₄	-53	74-75 ³

Remark: ¹From <http://www.chemtrack.org/MSDS.asp>

²At 10 mm Hg

³At 760 mm Hg

Amjoud et. al. [40] prepared the thin SnO₂ films by using of tetraethyl tin as precursor with deposition temperature between 320-470 °C. The results from energy dispersive spectroscopy, apart of deposited film at 320 °C contained some excess of Sn, it seems to be the uncompleted oxidation of the

precursor. At temperatures between 320-360 °C the films represented the columnar growth. When the temperature was increased to 360-440 °C, the films were well formed and faceted grains. The grains size was increased with the increasing of deposition temperature; it reached to 1 μm when the deposition temperature was 470 °C.

Amjoud et al. [43] studied the effect of tetraethyl tin molar fraction in vapor phase, it were between 2×10^{-4} - 1×10^{-3} . The grain size decreased with the increasing of tetraethyl tin composition in vapor phase, because it was affected by the higher nucleation rate of coating. Consequently, the SnO_2 films to be smoother and dense at high tetraethyl tin composition. Moreover, when the mean grain size and film roughness decreased, the film porosity will be decreased, that will decrease the electrical resistivity of the films.

2.9.5 Metal-organic chemical vapor deposition of iridium (Ir) and iridium oxide (IrO_2)

Iridium (Ir) and Iridium oxide (IrO_2) films have attracted much attention due to their excellent properties. Iridium is a noble metal with a small unit cell dimension, high melting point (2727 K) and good chemical stability. Due to its properties, iridium is a good diffusion barrier for oxygen. Iridium has a great interest as protective layer due to its good resistance against corrosion and oxidation at high temperature [4]. Iridium oxide films have excellent properties, especially their electrocatalytic properties and good stability in strong acidic solution for chlorine and oxygen evolution [33].

The several methods have been developed for preparing the Ir and IrO₂ films such as metal-organic chemical vapor deposition. There are some influences on the deposition of Ir and IrO₂ films, such as choice of precursors, deposition temperature and co-reactive gaseous, etc.

Because of the potential of Ir and IrO₂ films for some application, many types of Ir source precursors were studied for Ir and IrO₂ films coating by CVD. Initially, Ir(III) halides were used as precursor for Ir and IrO₂ CVD [4, 44]. Due to its low volatility and high decomposition temperature typically more than 800 °C [4], iridium halides were not good alternative. In addition, the corrosive and harmful atmosphere is generated during the decomposition of iridium halides.

Due to some drawbacks of iridium halides precursor, the organometallic iridium compounds are preferred for Ir film CVD. The iridium *tris*-acetylacetonate (Ir(acac)₃) and iridium *tris*-alkyl (Ir(C₃H₅)₃) complexes, are two commonly used as CVD precursors. For commercial available, Ir(acac)₃ is a better choice due to its excellent air stability. However, the high melting point and low volatility of Ir(acac)₃ has limited its development as the industrial standard [44].

In addition, other iridium sources reagents consist of Ir(I) metal complexes such as (MeCp)Ir(COD) [4, 45-49], Ir(COD)(acac) [50], [Ir(COD)(μ-OAc)]₂ [51], Ir(COD)(hfac) [52] and Ir(COD)(amak) [46] appear to be more useful for Ir and IrO₂ deposition due to their enhanced volatility and vapor phase transport properties which are uncomplicated by monomer-dimer equilibria. The physical properties of some Ir precursors are presented in Table 2-2.

Table 2-2 Physical properties of iridium CVD precursors

Compound	Melting point (°C)	Deposition temperature (°C)	Sublimation condition
$\text{Ir}(\text{acac})_3$	269-271	300-400	180-200 °C
$\text{Ir}(\text{C}_3\text{H}_5)_3$	Decompose at 65	100	50 °C/ 15 Torr
$(\text{MeCp})\text{Ir}(\text{COD})$	38-40	270-350	95 °C/ 0.05 Torr
$\text{Ir}(\text{COD})(\text{hfac})$	120	250-400	60 °C/ 0.05 Torr
$\text{Ir}(\text{COD})(\text{amak})$	127	350	50 °C/ 0.2 Torr
$[\text{Ir}(\text{COD})(\mu\text{-OAc})]_2$	135	250	125 °C/ 0.07 Torr

Maury and Senocq [4] studied on the deposition of Ir film by MOCVD in hot-wall CVD reactor by using $(\text{MeCp})\text{Ir}(\text{COD})$ as liquid Ir source. The influences of H_2 and O_2 addition, deposition temperature and residence time were obtained. In H_2 atmosphere, deposition of Ir film is very sensitive on the residence time and the decomposition temperature. Deposition started from 300 °C at residence time 0.05 sec. But, when increased deposition temperature to 400 °C, the Ir film abruptly deposited only a few centimeters from the entrance of the reactor due to the high reactivity of the feed gas mixture, which made difficultly control of film growth rate and uniform deposition along the reactor. With the presence of O_2 , the Ir films was dense when the thickness less than 100 nm, similar to surface morphology in presence with H_2 . However, the microstructure trended to be columnar when film thickness more than 1 micron. The coatings deposited using a high

excess of oxygen, $O_2/(MeCp)Ir(COD)$ of 1000, represented the mixture of Ir and IrO_2 . However, the co-deposition Ir and IrO_2 was not observed at $O_2/(MeCp)Ir(COD)$ molar less than 135. In addition, the film thickness gradient was observed with the increasing O_2 partial pressure. For high temperature and residence time, the growth rate is maximum at the entrance of the reactor, but rapidly decreases downstream. The better thickness uniformity can be obtained by optimization O_2 feed rate, deposition temperature and residence time that detrimental to the conversion rate of the precursor, subsequently, to achieve the mean growth rate along the reactor.

Chen et. al. [49] deposited IrO_2 on Si substrate in vertical cold-wall CVD reactor by using of $(MeCp)Ir(COD)$ as iridium source. The oxygen was used as both carrier and reactive gas. The supplying rate of oxygen is 100 sccm and oxygen pressure were 1, 10 and 30 torr. The deposition temperature ranged between 250 and 500 °C. At 1 torr, the high purity Ir film was obtained at temperature below 400 °C. At 450 and 500 °C, the rutile IrO_2 was detected. However, the diffraction signal due to the IrO_2 phase at 500 °C was diminished. At 10 torr, the Ir signal obtained at temperature ≤ 300 °C and the optimized temperature for growth of IrO_2 is between 400 and 450 °C. At 30 torr, the highly 101 orientation IrO_2 nanorods were deposited at temperature between 300-350 °C.