Chapter 5

General Conclusion

5.1 Electrode preparation

5.1.1 TiO_2 deposition by spray coating

Although the TiO_2 coating over SUS 316L produced by spray coating has uniform and good coverage. However, the TiO_2/SUS 316L was unsuitable for using as electrode for wastewater treatment by electrochemical oxidation due to its very short service life of TiO_2/SUS 316L and low adhesion of TiO_2 layer.

5.1.2 SnO_2 deposition by spray pyrolysis

Because of the uncontrolled drop size of precursor solution sprayed by a simple atomizer, the SnO_2 film coated by spray pyrolysis had inhomogeneous coating. Some precursor was incompletely decomposed from the unregulated substrate temperature. Due to its inhomogeneous SnO_2 coating, it could be mentioned that the spray pyrolysis was unsuitable to use for a production of SnO_2 specific electrode.

5.1.3 IrO_2 deposition by MOCVD

It was found that the IrO_2 film growth rate was affected by the O_2/Ir(acac)$_3$ molar ratio. With the increasing of O_2/Ir(acac)$_3$ molar ratio from 11,000 to 17,000, the maximum IrO_2 growth rate was decreased from 2.9 to 1.9 nm/min due to the higher Ir precursor concentration in

feed vapor. Furthermore, the $O_2/Ir(acac)_3$ molar ratio affected on the microstructure of IrO_2 film. The SEM and X-ray diffraction of IrO_2 film indicated that the columnar growth of IrO_2 with (101) orientation was observed at $O_2/Ir(acac)_3$ molar ratio of 17,000, while the dense IrO_2 film with (110) orientation was observed at the molar ratio of 11,000. The IrO_2 film had homogeneous microstructure and good coverage on Si wafer. However, the gradient deposition of IrO_2 film on Ti substrate was observed because $Ir(acac)_3$ had low volatility and difficultly controlled mass transfer. From the results, it concludes that the IrO_2 film from $Ir(acac)_3$ is not suitable for using as protective layer for SnO_2 specific electrode.

5.1.4 Ir deposition by MOCVD

Deposition of Ir film by using (MeCp)Ir(COD) as precursor with the presence of O_2 was investigated. It was found that the deposition of Ir film was strongly affected by deposition temperature and oxygen content in feed vapor mixture. The increasing of deposition temperature from 300 to 325 and 350 °C has significantly affected on the Ir deposition area. The deposition area was decreased from 13 to 11 and 9.75 cm from the entrance of the reactor, respectively. The growth rate of Ir film was very high at a few centimeters nearby the entrance of the reactor, but rapidly decreased downstream because the system was very active at high deposition temperature and the (MeCp)Ir(COD) was consumed immediately in a few centimeters from the entrance. When the $O_2/(MeCp)Ir(COD)$ molar ratio was 1545, the precursor was totally decomposed near the entrance of the reactor resulting the abrupt gradient film thickness. The maximum gradient was approximately 4 nm/min at 10 cm from the entrance and fell down to nearly zero after a few

centimeters. While the Ir film deposited uniformly over several centimeters long through the reactor when O_2/(MeCp)Ir(COD) molar ratio was 125 due to the reactivity of the system was reduced by decreasing of O_2/(MeCp)Ir(COD) molar ratio. The suitable Ir film to be used as the protective layer for specific electrode was deposited at 300 °C, total pressure of 12 Torr and oxygen molar ratio of 125.

5.1.5 SnO_2 deposition by MOCVD

The SnO_2 coatings were uniform and exhibited good conformal coverage. The increasing O_2/TET molar ratio from 300 to 1,200 was not great influence on the growth rate of SnO_2 in first 10 cm. However, the O_2/TET molar ratio at 300 presented the higher growth rate of SnO_2 film after passed 10 cm. The growth rate of SnO_2 film is a function of TET concentration in feed gas composition. The increasing of TET concentration in feed gas mixture has no influence on the microstructure of SnO_2 film. The substrate materials have no affected on SnO_2 film growth rate. However, the SnO_2 film growth rate could be improved by the substrate with high surface roughness due to its higher specific area. The SEM images show that the SnO_2 film was dense, smooth, homogeneous microstructure and uniform coverage deposition on the high surface roughness substrate. The suitable SnO_2 active coating for using as anode organic pollutant degradation was deposited at 380 °C, 15 Torr of total pressure and O_2/TET molar ratio of 1,200.

5.2 Application of specific electrode for restaurant wastewater treatment

5.2.1 Application of specific electrodes in batch process with model solution

From the application of $SnO_2/Ir/Ti$ specific electrode for oxalic acid destruction, it was found that the SnO_2 thickness does not have the great influence. It may be cause by the production of adsorbed hydroxyl radicals was occurred only at the surface of electrode. While the increasing of current density from 5 to 10 mA/cm^2, leads to less degradation rate of oxalic acid by electrochemical oxidation due to the characteristic of diffusion-controlled processes. In such system, the increasing of current density cannot increase the organic removal efficiency, but only favors the anodic side reaction. In case of SnO_2/Ta and $SnO_2/TaC/Ta$ electrodes, Ta substrate was brittle and lose some physical properties after etched by HF resulting on the brittle electrode. While the passivation of SnO_2 film from $SnO_2/TaC/Ta$ after a few minutes in electrochemical characterization that affected by some free carbon between SnO_2 film and TaC surface.

5.2.2 Kinetic investigation for batch process with model solution

The kinetics of TOC degradation on $SnO_2/Ir/Ti$ occurs as a two-step process. Firstly, when the solution contains the high TOC concentration, the kinetic was the zero-order with respect to TOC of model solution.

$$TOC_t = TOC_i - k_0 t$$

The other one, at low TOC concentration, the kinetic was the first-order with respect to TOC concentration in model solution.

$$TOC_t = TOC_{t*} \exp\left[- k_1 (t - t^*)\right]$$

When $t^* = 120$ min., $k_0 = 1.1855$ mg/L-min and $k_1 = 0.0017$ min^{-1}.

5.2.3 Application of specific electrodes for actual restaurant wastewater

Similar to the degradation of organic pollutants in batch process, TOC removal efficiency on $SnO_2/Ir/Ti$ is higher at 5 mA/cm^2, then decreased when increased current density to 10 mA/cm^2 which indicated to a weak behavior is the characteristic of diffusion-controlled processes. The increasing of residence time is not proportional increase of TOC and COD removal. That, increases from around 55 to 62 % for TOC and 54 to 62 for COD with an increase in the residence time from 2 to 3 hr due to the fast step of reaction with zero-order reaction occurred in 2 hr. Then, the reaction was changed to slower step with first-order reaction respects to the TOC concentration in wastewater. Similar to the pollutant degradation of organic pollutant in batch experiment, it shows that the SnO_2 active layer thickness was not a great influence on the TOC removal efficiency due to the adsorbed hydroxyl radicals for organic pollutant degradation were produced only at the surface of electrode.

From these results, it should be concluded that the specific $SnO_2/Ir/Ti$ prepared by metal-organic chemical vapor deposition is powerful for the degradation of organic pollutant presented in wastewater by electrochemical oxidation.