

# CHAPTER I INTRODUCTION

The combustion of fossil fuel in factory and automobile engines mainly emit CO, NO<sub>x</sub> and SO<sub>2</sub>, causing environmental problems, and vitally affecting human heaths. Due to these increasing pollutants, a better process control and a new generation of gas sensors are desired. Normally gas sensor devices employ metallic oxide such as SnO<sub>2</sub> or ZnO as sensing materials. However, they require operating at 300 °C or above (Miasik, 1986). On the other hand, a conductive polymer can detect a gas and operates at room temperature.

#### Background.

### 1.1 Conductive Polymer

In 1977, the first conductive polymer, the doped polyacetylene was reported. The conductive polymers are generally composed of conjugated monomer units with  $\pi$ -electrons delocalized along the  $\pi$ -conjugated back bone. Figure 1.1 shows the repeating units of some types of conductive polymers, such as trans-polyacetylene, polyaniline, polypyrrole, and polythiophene (Kohlman *et al.*, 1996).

$$(a) \qquad (b) \qquad (c) \qquad (d)$$

Figure 1.1 The repeating units of (a) trans-polyacetylene, (b) polypyrrole, (c) polythiophene, and (d) polyanilene.

The electrical conduction of conductive polymer is caused by the delocalization of charge carriers, formed by donating or withdrawing electrons from polymer chain via a reduction or oxidation reaction. This electron transition is known as doping process: p-type doping and n-type doping. In p- type doping, oxidizing

agents remove electrons from the valence band, generating the positive charges which can delocalize as charge carries. In n-type doping, reducing agents add electrons to polymer chains, generating the negative charges which can delocalize as charge carriers. The p- type doping conductive polymer is more thermodynamically stable than the n-type one (Ruangchuay, 2003).

The another term of charge carrier species is the polaron and bipolaron. Polaron, formed during the oxidation process, is a form that has a free radical and a positive charge on the chain. When a concentration of polaron is high, two of the radicals in particular two polarons combine each other to from a covalent bond. This form of charge carriers consists of two positive charge remaining from the combination of those two polarons. It is called the bipolaron. These charge carriers are stabilized by ions from the reaction medium, called dopant. The conductivity of the polymer is varied by changing type and concentration of dopant (Ruangchauy, 2003).

# 1.2 Polypyrrole

Polypyrole (PPy), one of conductive polymers, has been found to have some applications in the gas sensing technology because it exhibits excellent thermal and electrical properties, fulfills all of requirement of an ideal conductive polymers, and it can be synthesized easily (Prissanaroon, 2000). PPy is normally polymerized by either an electrochemical method (Fink, 1986) or a chemical method (Appel, 1996). However PPy has low selectivity, poor mechanical property, and inefficient solubility. To improve these disadvantages, many fundamental studies have been conducted (Benseddik, 1995, Heurberger, 1995, Cheah, 1997).

### 1.3 Zeolites

Zeolites are crystalline hydrated aluminosilicates of group I and group II elements, Li, Na, K, Rb, Cs, Mg, Ca, Sr, and Ba. Structually, a zeolite is a framework of aluminosilicates which are based on in a finite extending three-dimensional network of AlO<sub>4</sub> and SiO<sub>4</sub> tetrahedra linked to each other by sharing of

oxygens (Beck, 1973). Their corners link these polyhedra to produce an open structure that has internal cavities in which molecules of various sizes can be trapped. These internal voids, modified to have specific opening size ranges, trap and hold a variety of molecules that enter the structure matrix (Dyer, 1993).

Zeolites have played a major role in the development of absorption and gas separation technology. The separation of gas mixture by the zeolites are affected by (Auerbach, 2003):

- 1. Size or steric exclusion of certain components of a gas mixture from entering the zeolite pores, whereas the other components can enter the pores and are adsorbed.
- 2. The thermodynamic selectivity, which is a quantitative measure of the preferential adsorption of certain components over others when all components can enter the pores.
- 3. Kinetic selectivity, which is a quantitative measure of the ability of certain components to enter the pores faster than other components.

The majority of gas separation by zeolite use mode 2. Thermodynamic selectivity for adsorption of a particular gas inside a zeolite cavity is generally made possible by preferential adsorption of that gas on accessible cationic sites inside the crystal. The strength and selectivity of adsorption of a gas on a zeolite depends on the size, shape, and structure of the zeolite cavity, cationic charge density, concentration of cations, polarizability, and permanent polarity of the guest absorbate molecules (Auerbach, 2003).

### 1.4 The Air Pollutants

## 1.4.1 Carbon Monoxide (CO)

The incomplete combustion of carbon-based fuels generates carbon monoxide, a colorless and odorless gas. The concentration of CO in the atmosphere is dependent on time of day, location, weather, and human activities. CO levels tend to be highest in areas of crowed traffics (Hay *et al.*, 1987).

When the concentration of CO exceeds 100 ppm, It may causes nausea, headache and dizziness. The toxicity of CO lies in its unusual ability to bind strongly to hemoglobin, the oxygen carrier in blood (Chang, 1994). The affinity of hemoglobin to CO is about 200 times greater than that of O<sub>2</sub>. Hemoglobin molecules with tightly bound CO cannot carry the oxygen needed for metabolic processes.

## 1.4.2 Nitrogen Oxide (NO<sub>x</sub>)

The burning of fossil fuels in furnaces and automobile engines raises the gas temperature sufficiently to converse  $N_2$  and  $O_2$  in to  $NO_x$  (O'Neil, 1993). About 90 percent of all  $NO_x$  emissions is in the form of NO. However, in the presence of sunlight, ozone and hydrocarbon, NO can be quickly oxidized to  $NO_2$  (Hay et al.,1987).

The conversion of NO to NO<sub>2</sub> in the atmosphere is one of reactions that cause three environmental problems: a photochemical smog, an acid rain and a decomposition of ozone (O'Neil, 1993).

#### 1.4.3 Sulfur Dioxide (SO<sub>2</sub>)

The majority of SO<sub>2</sub> emissions is attributable to the combustion of fossil fuels in the stationary facilities. Coal combustion is responsible for approximately 68 percent of total SO<sub>2</sub> emissions, compared with 11 percent for oil, and less than 1 percent for natural gas (Hay *et al.*, 1987).

SO<sub>2</sub> is the major sources of acid rain in the environmental. The acid rain causes the irritation to living things and the corrosion of buildings. At the level of about 250 ppm in a 24 hour duration, SO<sub>2</sub> causes the bronchitis, an illness that affects the bronchial tubes to the lung. At the level over 500 ppm in a 24 hour duration, its causes the asthma, an illness that causes the difficulty in breathing. The sudden death occurs when the levels of SO<sub>2</sub> is over 750 ppm (O'Neil, 1993).