

CHAPTER II

LITERATURE SURVAY



2.1 Polyaniline and Doped Polyaniline

MacDiarmid *et al* (1985) showed that polyaniline can be synthesized chemically or electrochemically in an aqueous acidic condition. The insulating form of polyaniline was doped in dilute aqueous protonic acids to obtain the conducting form ($\sigma = 5 \text{ S/cm}$). Both insulator and conductive forms were stable in the presence of air and/or water. The conducting form of polyaniline can also be reversed to the insulating form by the treatment with an aqueous alkali solution. In the same year, MacDiarmid *et al.* (1985b) reported an excellent cathode characteristic of polyaniline including recyclability between the quinoid-benzenoid-diimine form and the iminium salt form. A zinc anode and PbO₂ cathode was used with a rechargeable battery cell.

Palaniappan *et al.* (1994) investigated the thermal stability of the chemically synthesized polyaniline salts, using the thermal analysis and spectral methods. Polyaniline salts underwent a three-step weight loss process in the heating cycle. The first step corresponded to the loss of water molecules from the polymer chain. In the second step, a small amount of acid escaped as a volatile gas, and the last the polymer underwent an oxidative thermal degradation.

Doping process is an important process that induces a transition from an insulation state to a conductive state. It can be achieved by introducing the dopant molecules into polyaniline chain. In recent years, polyaniline and its derivative have become a prototype system for the study of electrical properties due to its intrinsic redox properties. Kang *et al.* (1995) studied the protonation and deprotonation of polyaniline films and powders. In their work, the change in intrinsic oxidation state of emeraldine base as a function of treatment time in aqueous acid was measured through the technique of XPS. It was concluded that the treatment time increased as the intrinsic redox state ($[\text{=N-}]/[\text{-NH-}]$) decreased for all types of acid. There are many researches that studied the effects of dopant type, dopant amount, and doping method on PANI. One study used macromolecular acids such as sulfonated PS, PPO and PEEK to dope PANI (Geng *et al.*, 1997). They found that the conductivity of the

doped PANI depended on the solution concentration, preparation method and structure of the macromolecular acid used. PANI doped with a macromolecular acid also showed a higher environmental stability than that doped with a small molecular acid. Another work was done by Yin *et al.* (2000); they polymerized a PANI in the presence of dodecylbenzene sulfonic acid co-doped with HCl. Aniline dodecylbenzenesulfonic acid stimulated the solubility while aniline hydrochloride enhanced the conductive structure of the synthesized polymer. A co-doped PANI with high conductivity was obtained without any additional doping. At an ANIHCl/ANIDBSA molar ratio of the feed of 3:7, the polymer showed σ equal to 7.9 S/cm and a maximum yield of 30.8 %.

The formation of polyaniline and nature of its structures have been studied by many researchers. Stejskal *et al.* (1996) used spectroscopic method to correlate the color with its conductivity. They found that the oxidative polymerization of aniline gave a polyaniline differing in electrical conductivity and in color. They also proposed a scheme of interrelated structures, which accounted for all the spectroscopy and conductometric observations, along with a set of equations summarizing the chemical transformation.

2.2 Polyaniline as Gas and Chemical Vapor Sensors

Jiakun *et al.* (1993) investigated and found that polyaniline has a high sensitivity to NH_3 gas at normal temperature, with a good selectivity over H_2 and O_2 , and a good reliability. The resistance increased because NH_3 molecules acted as donors after absorbing on the surface of the sample, in addition to forming an electric barrier on the surface of the sample.

Amrani *et al.* (1995) reported that electrically conductive polymers could be used for detecting vapors and gases by measuring the reversible change in the DC resistance. The sensors had a very broad chemical specificity with a higher sensitivity to polar materials. The results demonstrated a quantification of concentration and a discrimination between the chemicals tested on the basis of capacitance, conductance, resistance, and dissipation factor as functions of frequency.

In 1997, Larenfeira *et al.* demonstrated that a thin PANI film through a chemical synthesis deposited on a acrylic substratum and two graphite electrode surfaces could be used to determine ammonia concentration in a fertilizer. The conductance of the PANI film decreased with ammonia concentration when exposed to ammonia gas. The detection range of the system was 0.6-3.7 $\mu\text{g}\cdot\text{mL}^{-1}$ with a response time of 4 minutes and a relative standard deviation of about 5%. The advantages of this system were low operational cost, simplicity in operation, good sensitivity, precision and accuracy, and a low sampling processing.

In 1998, Conn *et al.* reported the fabrication and sensor properties of polyaniline-platinum oxide chemoresistor in the presence of combustible gases and CO. Prior conditioning of the sensors in a H_2 atmosphere resulted in an increased selectivity for H_2 in air at concentrations between 1,000 and 5,400 ppm. The conducting sensors showed a negligible response to hydrocarbons and CO. The H_2 sensing properties were believed to be due to the reduced state of PtO_2 (i.e. PtO_2 -PtO).

In 2000, Prissanaroon *et al.* studied the electrical conductivity response of dodecylbenzene sulfonic acid-doped polypyrrole films to SO_2 - N_2 mixtures. The authors found that the temporal response of conductive polypyrrole films was improved with increasing doping level. Above critical doping level, the sensitivity of PPy films when exposed to SO_2 depended on the dopant concentration used and could be correlated with morphology of PPy. The conductive polymer chains changed from assuming tree dimensional random-coil structures to rod-like fibrillar structures.

2.3 Zeolite

2.3.1 Synthesis of AlMCM41

In 1992, researchers at Mobile R&D Corporation discovered a new silicate/aluminosilicate mesoporous molecular sieve family with exceptionally large pore structures (Beck *et al.*, 1992a; Kresge *et al.*, 1992a). Depending on the synthesis conditions, they obtained materials consisting of a hexagonal phase known as MCM41, a cubic phase known as MCM48, or a non-stable lamellar phase

(MCM50) which can be stabilized by a post synthesis treatment with tetraethylorthosilicate.

The synthesis of AlMCM41 was first developed by Ryoo et al. (1995). The authors reported the synthesis of highly ordered MCM41 by adding acetic acid to the reaction system in order to shift the equilibrium between the reactants and the mesophases towards a desired direction. The addition of the acid was proposed to neutralize the hydroxyl and to shift the equilibrium in the positive direction.

Ryoo *et al.* (1997) studied the distribution of framework alumina in a mesoporous molecular sieve MCM41 with various steps in the synthesis process. The framework aluminum became homogeneously distributed inside the resultant MCM41 particles if sodium aluminate was added to the reaction mixture, consisting of an aqueous solution of hexadecyltrimethylammonium (HTA) chloride and sodium silicate prior to the formation of the surfactant-silicate mesostructure. The framework alumina could be incorporated into the outer region within MCM41 particles if aluminum source was added after the formation of mesostructure was complete.

2.3.2 Application of Zeolite as Gas Adsorption

Lee *et al.* (1996) investigated the characteristics of CO gas adsorption on chemically treated natural zeolite. They observed that an acid treatment was more effective than an alkaline treatment in the liquid adsorption because the exchanged H^+ ion attributed to the enlargement of pore size. However, in the gas adsorption, the amount of CO was higher when treated in 5N NaOH ~ 0.011 g than that when treated in 5N HCl acid solution ~ 0.017 g. In the HCl treated zeolite, the high portion of micropore ~10 Å led to a hindrance of gas diffusion rate. In the NaOH treatment, in which the pore and surface areas decreased, an increase in the gas adsorption amount could be related to the exchanged Na^+ ions locating on the surface and serving as an adsorption site.

Fukui and Nishida (1997) found that Ferrierite, one of siliceous zeolite, had a prominent ethanol filtering effect. It was coated on the CO selective gas-sensor based on La_2O_3Au/SnO_2 ceramics, a high selectivity to CO among H_2 ,

CH₄, i-C₄H₁₀ and C₂H₄, while a high sensitivity to C₂H₅OH. Ferrierite acted as an acidic catalyst layer converting C₂H₅OH into C₂H₄ with a low sensitivity by dehydration. The prominent performance was related to a strong acid strength and a large acid amount; moreover, the siliceous zeolite had a hydrophobic property, a large specific area and good thermal stability. As a result, a CO selective gas sensor with sensitivity to CO over ten times higher than those of other gases.

Frisch, *et al.* (2001) determined the morphology, DC conductivity and their effects on the paramagnetic properties of the PANI when it was prepared with a presence of zeolite 13X. They found that the morphology between the pure PANI and the zeolite/PANI sample were similar, but the interconnectivity of granules in the sample containing zeolite was rather poor. Because zeolite pores in the polymerization hindered chain overlap, the DC conductivity exponentially decreased with increasing zeolite content.

Limtrakul *et al.* (2001) examined the interaction of CO with H-ZSM5 and Li-ZSM5 zeolites using quantum cluster and embedded cluster models. For the H-ZSM5 and Li-ZSM5 zeolites, the C-bound complex was found to be more stable than the O-bound complex. Increase in acidity of the Bronsted acid site increased the number CO-binding sites of these complexes.

2.4 Polyaniline/Zeolite Composite

Enzel *et al.* (1989) designed a model system via an encapsulation of polymeric chain conductors in low-dimensional, ordered lattice of a zeolite in order to reduce the size of electronic circuitry to molecular dimension. Polyaniline was synthesized in the channels of mordenite (one-dimension) and zeolite Y (three-dimension). The results showed that the polyaniline chains in mordenite channels appeared to be more highly oxidized than in zeolite Y. The conductivity of zeolite/polymer samples ($< 10^{-8}$ S/cm) was lower than the bulk conductivity of undoped polyaniline ($\approx 10^{-6}$ S/cm). The level of intrazeolite reaction or the nature of the channel system controlled the degree of polymer oxidation.

Wu and Bein (1994) prepared conducting filaments of polyaniline in a three-nanometer wide hexagonal channel system of MCM-41. The oxidative

polymerization occurred by an adsorption of aniline vapor into the dehydrate host. Spectroscopic data showed that the filaments were in the protonated emeraldine salt form, and chromatography indicated chain lengths about 190 aniline rings. The significant low-field conductivity of the polymer filaments as measured by microwave absorption at 26 GHz demonstrated that the conjugated polymer could be encapsulated in nanometer channels and still supported mobile charge carrier. This demonstration represented a step toward the design of nanometer electronic devices.