

CHAPTER II

LITERATURE SURVEY

2.1 Synthesis of Polyaniline

Polyaniline has attracted much attention since MacDiarmid *et al.*, 1985 reinvestigated this material as conducting polymer. Polyaniline can be synthesized by electrochemical and chemical oxidative polymerization. The synthesized form, as emeraldine base, is an insulator. This form can be changed to conducting form either by protonation with a protonic acid or by charge transfer with an oxidation agent.

Huang *et al.* (1986) synthesized emeraldine base form of polyaniline as a film by using the electrochemical oxidative polymerization. This film exhibited fibrillar morphology. They proposed that the emeraldine salt have a symmetric conjugated structure having extensive charge delocalization. Shortly after this study, Cao *et al.* (1989) presented results on the effect of the chemical oxidative polymerization conditions on the viscosity and electrical conductivity of polyaniline.

Stejskal *et al.* (1996) 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 observation and a set of equations summarizing the chemical transformation.

2.2 Acid Doped Polyaniline

Xia *et al.* (1994) demonstrated that HCSA fully doped polyaniline chain had a more expanded coil-like conformation and a longer conjugated length in m-cresol, p-cresol, 2-chloroform, 2-fluorophenol and 3-ethylphenol than in chloroform, NMP, DMF and benzyl alcohol. The coil-like conformation can be irreversibly converted to the expanded coil-like conformation by an exposure to m-cresol vapor at room temperature. They also found that the conductivity of expanded coil-like of PANI chain was high (~200 S/cm) because of higher charge carrier mobility.

Palaniappan *et al.* (1994) investigated the thermal stability of five different PANI salts including PANI-H₃PO₄, PANI-H₂SO₄, PANI-HCl, PANI-TSA, and PANI-HCOOH. Polyaniline salts undergoing a three-step weight-loss process in the heating cycle: loss of water or solvent (up to 110°C), dedoping and decomposition (after 275°C) and those depended on the counterions.

Avlyanov *et al.* (1995) investigated the conformation changes and doping level of polyaniline-camphosulfonic acid in m-cresol or chloroform. Viscosity measurement as a function of increasing m-cresol content in the mixed solvent and increasing protonation level of EBH⁺/CSA⁻ in m-cresol, indicated that the fully protonated polymer adopted a maximized expanded molecular conformation in a good solvent such as m-cresol. These results suggest that the different conductivity resulted from its different molecular conformation. Later, Luzny and Banka (2000) showed that the conductivity of films not only depended on conformation changes, but also their degree of crystallinity.

Zhang and MacDiarmid (1995) reported that the molecular conformation of doped polyaniline was strongly affected by its protonation level in pure acid solution. In the strong acid, both imine and amine nitrogen atoms of polyaniline were protonated, resulting in an expanded coil molecular conformation. In a weak acid, only the most basic imine nitrogen atoms were protonated, resulting in a compacted coil conformation.

Zeng and Ko (1998) studied the structure, doping, conductivity, and thermal stability of the reduced polyaniline (PANI-R) using hydrazine as the reactant. It was found that when PANI-R was doped with HCl and iodine, only the iodine-doped product showed high electrical conductivity. Because some of benzenoid unites in PANI-R were oxidized to quinoid units during iodine doping process, a highly conjugated system might be found in PANI-R chains.

Li and Wan (1999) studied the stability including thermal stability and conductivity stability in air and after thermal treatment of polyaniline films prepared by doping-dedoping-redoping method. This method was shown to improve the thermal stability of doping-PANI films. The thermal stability in the decreasing order of PANI-H₃PO₄>PANI-p-TSA>PANI-H₂SO₄>PANI-HCl>PANI-HPO₄>PANI-CSA

was observed. The conductivity at room temperature was reduced after thermal treatment, it was dependent of the counterions. The conductivity of doped-PANI film placed in air decreased slowly with time due to deprotonation and it also depended on the counterions.

Lee *et al.* (1999) prepared the PANI membrane that only O₂ could permeate through the membrane while N₂ cannot. A PANI composite membrane was prepared with a nylon porous support membrane by solvent welding. PANI composite membranes were doped, dedoped and redoped with different degrees of doping level. After doping and dedoping process, the permeability of a doped PANI membrane decreased and selectivity slightly increased because of changes in morphology of PANI. As redoping continued, the degree of doping increased while the d spacing decreased, resulting in a dramatic increase in selectivity.

2.3 Polyaniline as Gas Sensors

Jiakun *et al.* (1993) investigated and found that polyaniline had a high sensitivity to NH₃ gas at normal temperature accompanied with low resistivity, good selectivity, and reliability. The resistance augmented with the number of electron holes because NH₃ molecules acted as donors after being absorbed, and formed an electric barrier near the surface of the sample.

Agbor *et al.* (1995) showed that polyaniline could be deposited onto a substrate as finely thin films which the thickness per layer as thin as 5.5 ± 0.6 nm. Exposing a single LB layer of polyaniline to NO₂ and H₂S led to the increasing of reflectivity and resonance angle. The effects were partly reversible, with lower detection limits of about 50 vapor part per million at room temperature.

Dhawan *et al.* (1997) showed that the leaching of the protonic sites in the doped polyaniline grafted surface on exposure to aqueous ammonia led to a change in resistance of the polymer. The surface resistance changed from 102 to 1010 Ohm. This aspect can be utilized in the designation of a chemical sensor for aqueous ammonia.

Kang *et al.* (1999) pointed out that the electrical conductivity of polyaniline doped with HCl decreased upon an exposure to oxygen and increased reversibly

reversibly upon evacuation. It was concluded that the decrease in conductivity arose from the reduction in both the concentration and mobility of polarons, the charge carrier for electrical conductivity. This result was investigated by electron paramagnetic resonance (EPR). However, the decrease in the electrical conductivity was very small whereas the decrease in the polaron concentration was large. It was also found that the time scale for oxygen diffusion was much longer than that for the reaction of oxygen with polaron. Therefore, the decrease in electrical conductivity might be associated with the reduced mobility instead of the reduced concentration of polaron.

Bao *et al.* (1999) presented the behavior of the resistance of fully doped PANI derivatives as a function of pressure at room temperature. It was found that the resistance of sample as a function of pressure depended on the interplay between increased interchain transfer due to increased pressure and the decreased transfer rate due to smaller localization length. High values of the resistance at ambient pressure as the substituent group along the main chain PAN backbone became larger are consistent with measurements of dc conductivity on the same samples.

2.4 Zeolite and Polyaniline/Zeolite Composite

Lee *et al.* (1996) investigated the characteristics of CO gas adsorption on chemically treated natural zeolite. They observed that acid treatment was more effective than the alkaline treatment in liquid adsorption because the exchanged H^+ ion attributed to the enlargement of pore size. However, the amount of CO adsorbed was higher in the 5N NaOH than in the 5N HCl treatment. For the HCl treated zeolite a high portion of micropore $\sim 10 \text{ \AA}$ led to hindrance of gas diffusion rate. In the NaOH treatment, though the pore and surface area decreased, an increase in the gas adsorption amount could be attributed to the exchange Na^+ ion located on the surface serving as an adsorption site.

Fukui and Nishida (1997) found that Ferrierite, one of siliceous zeolite, had a ethanol filtering effect. It was coated on the CO selective gas-sensor based on La_2O_3Au/SnO_2 ceramics. This sensor had a high selectivity to CO and C_2H_5OH

among combustible gases. Ferrierite acted as acidic catalyst layer converting C_2H_5OH into C_2H_4 a low sensitivity by dehydration. The performance was related to a strong acid strength and a large acid amount. As a result, a CO selective gas sensor with sensitivity to CO over ten times higher than that to the other gases was obtained at 300°C.

Frisch, *et al.* (2001) determined the morphology, DC conductivity and effect on the paramagnetic properties of the PANI when it was prepared with the presence of zeolite 13X. They found that the morphology between the pure PANI and the zeolite/PANI sample are similar, but the interconnectivity of granules in the sample containing zeolite is 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 zeolite 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 O-bound complex. Increases in acidity of the Bronsted acid site and CO-binding energy of these complex resulted from inclusion of the Madelung potential from the zeolite framework.

Catana *et al.* (2001) used FT-IR and EPR of adsorbed probe molecules to study Lewis acid sites in zeolite with different nonframework Al content. The Lewis acid sites were identified by FT-IR of adsorbed CO at low temperature and by EPR of adsorbed NO. In both cases, the spectroscopic results could be related with the strength and the number of Lewis acid sites.