

## CHAPTER II LITERATURE SURVAY



### 2.1 Electronic Structure of Polypyrrole

Brédas *et al.* (1983) presented the first-principle calculation on the geometric and electronic structures of undoped and doped Ppy chains, indicating the appearance, upon a high doping, of the bipolaron state in the gap. A conductivity mechanism based on the motion of spinless bipolarons was consistent with the absence of ESR signal in the electrochemically cycled highly conducting Ppy.

Nechtschein *et al.* (1986) conducted an electrochemical polymerization of Ppy to investigate the polaron and bipolaron formations in Ppy. The result showed that the energy required for creating a bipolaron was about the same as for creating two polarons. The non-Nernstian behavior, the non linear relation between the applied potential and the amount of charges that occurs during the electrochemical polymerization observed for the redox process, was explained by the introduction of the interparticle charge repulsion interaction.

In 1986, three research groups, Fink and Scheerer [1986], Wernet *et al.*[1986], and Freund and Gonska [1986], studied the electronic structure of Ppy-based conducting polymers by using the high-resolution electron-energy-loss spectroscopy and electron diffraction. The evolution of the  $\pi$ -electron band structure as a function of oxidant can be explained in terms of a bipolaron model. Strongly oxidized Ppy is not a metal, but it has narrower bands in the gap which can be assigned as the bipolaron bands. The dielectric functions of electrochemically reduced Ppy films were well described by a linear-combination of atomic-orbital-complete-neglect-of-differential-overlap calculation on oligomers (Fink *et al.*, 1986). The treatment of as-grown oxidized Ppy films by alkali metals led to almost neutralized but not the n-type dopant films. The treatment of oxidized Ppy with NaOH did not change the  $\pi$ -electron band structure on the carbon atom but led again to a reaction on nitrogen atoms. Moreover, the XPS and ultraviolet photoelectron spectroscopy data of perchlorate-doped Ppy and tosylate-doped Ppy studied by Bätz

*et al.* (1991) showed that the valence-band structure of the latter agreed with the theoretical expected features for a one dimensional polymer. The finite density of the state at Fermi energy was in accordance with polaronic bands modulated by Coulomb repulsion, as well as with a disorder-induced destabilization of Peierls ground state (Bätz *et al.*, 1991).

## 2.2 Chemical Synthesis of Polypyrrole

Lee *et al.* [1995] used a chemical polymerization process to synthesize Ppy dope with DBSA. The polymer was soluble in *m*-cresol and conditionally soluble in chloroform, dichloromethane, or 1,1,2,2-tetrachloroethane. Soluble polypyrrole showed the same FT-Raman scattering and UV-light absorption spectra as those of electrochemically polymerized Ppy. The solution of polymer in chloroform was cast to a stiff film with a very smooth surface and the electrical conductivity of the film was 5 S/cm.

Ppy doped with arylsulfonate was synthesized by a chemical route (Thiéblemont *et al.* 1995). From the thermal analysis, at high temperature ( $T > 230$  °C), the oxidation appeared to be a bulk phenomenon, which led to the decomposition and complete combustion of the polymer. At moderate temperature ( $T < 230$  °C), the oxidation was a slow and gradual process, most likely limited by O<sub>2</sub> diffusion in the oxidized material. The kinetics of this oxidation process was determined and its activation energy was evaluated to be about 110 kJ mol<sup>-1</sup>.

For the chemical synthesis method, the experimental result of Appel *et al.* (1996) showed that the best initial monomer concentration was about 0.4-0.5 M, and less than 0.1M of oxidant should be added instantly to achieve a high electrical conductivity. Moreover they studied the technique that employed a coating of thin film on a non conductive substrate. They found that by exposing an oxidant/dopant solution to pyrrole vapour, a very thin and highly conductive film could be obtained.

The *in situ* doping polymerization of Ppy, using  $\beta$ -naphthalene sulfonic(NSA) acid as dopant, was carried out by Shen and Wan (1997). The polymer could be dissolved in *m*-cresol because NSA reduced intermolecular and intramolecular interactions between Ppy chains, and prevented the crosslinking

among Ppy chains during the polymerization process. The product exhibited a fibrillar morphology. Casinol et al.(1997) also used in situ doping polymerization to synthesize Ppy. In their reaction medias,  $\text{FeCl}_3$  and  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  acted as oxidants, and paratoluenesulfonic (TS) acid and naphtalnesulfonic (NS) acid acted as dopants. They found that Ppy, doped with TS, exhibited the highest conductivity and thermal stability. The conductivity had remained constant for over 14 days. The moisture content in Ppy, affecting the conductivity, was investigated. When the moisture content in Ppy increased, the conductivity of Ppy increased and vice versa. Due to water molecules, they could ionize the NH groups in Ppy, causing number of charge carriers to increase.

### 2.3 Electrical Conductivity of Polypyrrole

An enviromentally stable study of Ppy/poly(vinyl alcohol)(PVA) was conducted by Benseddik *et al.*(1995). The XPS study showed that a strong oxidation occurred upon aging with the formation of bonds such as C=O, and possibly COOH and COOR at the chain end. The strong aging effect by oxidation was the most probable cause to explain the decrease of the conductivity observed in the samples, whereas the PVA matrix also might have played an important role. Therefore, it should be interesting to perform similar measurement in conducting Ppy prepared as a composite with another matrix.

Child and Kunh (1997) proposed that the stability of Ppy coating could be enhanced significantly with an addition of 2,4-dihydroxybenzophenone into the reaction mixture. This additive did not serve as a dopant, but was used in conjunction with arylsulfonate dopants. The conductivity of Ppy coated fabrics, containing DHBP, displayed a dramatic increase during short aging times at elevated temperatures. The magnitude of this annealing effect was dependent on the film thickness, the aging temperature, and the amount of DHBP introduced. Cheah *et al.* (1997) investigated the thermal stability of Ppy. From the result of their experiment, a slight increase in conductivity was observed for acid treated Ppy films which was found to be due to the protonated pyrrole structure. This effect was dramatically enhanced by a treatment at high temperature where an increase in conductivity of

more than 84% could be achieved. Base treatment of Ppy film resulted in the decomposition of pyrrole structure leading to the loss of conductivity (<40%). Preliminary XPS results indicated that both acid and base treatments resulted in the elimination of reactive sites for oxygen. Long term thermal aging of these treated films were conducted at 150 °C in air. The conductivity decay behavior was found to follow multiple first order chemical reaction kinetics.

Gilani and Ishiguro (1997) stated that the stretched  $\text{PF}_6^-$ -doped Ppy had low resistivity due to the increase in the interchain transfer of charge.

In 1998, Fedorko and Skákalová concluded that there was an unusual low pressure dependence of electrical conductivity in the  $\text{BF}_4^-$ -doped Ppy. The reversibility, glass transition, piezochromism, IR spectra and analogy with similar effects in polythiophene supported a coil-rod conformational transition effect which could explain the hysteresis observed. From a practical point of view, one should be aware that, if there was an uncertainty in pressure control, the effect could appear in usual electrical conductivity experiment with Ppy as chemical gas sensors. Potentially, the effect could be interesting in a low pressure detection.

Based on the XRD and conductivity results, the increase in short range ordering in polymer film increased conductivity but not conductivity stability, which was governed by other chemical changes (Cheah *et al.*, 1999).

Ando *et al.* (2001) studied the electrical conductivity changes of Ppy and polythiophene films with a heat treatment. From room temperature to 150 °C, the conductivity of Ppy film remained constant. From 150 to 300 °C the conductivity dropped due to the decomposition of Ppy and the loss of dopant ion ( $\text{ClO}_4^-$ ). Above 300 °C, the conductivity increased again. Above 750 °C, the conductivity was higher than that of the original film due to the formation of a carbonaceous material.

## 2.4 Polypyrrole as Gas and Chemical Vapor Sensor

In 1989, Gustafsson *et al.* studied interactions between  $\text{NH}_3$  and Ppy. There are two interaction types, reversible and irreversible interaction that was interpreted by the change of electrical properties of Ppy treated with  $\text{NH}_3$ . The irreversible change occurred when the materials were exposed to high concentration

of  $\text{NH}_3$  for along period of time due to the formation of amide-type carbonyl groups, amine groups, and ammonium ions.

Jonathan *et al.* (1992) studied polypyrrole doped with bromine as gas and vapor sensors. The polymer was exposed to methanol, hexane, 2,2-dimethyl butane, ammonia, and hydrogen sulfide. They found that the resistance change of polypyrrole was due to a mixed response involving electronic effect and physical effect. The electronic effect was caused by the transfer of electrons between the gases and the polymer chains. The physical effect was caused by the swelling of polymer due to vapor acting as a solvent.

Nagase *et al.* [1993] studied the response of Ppy to organic vapors by varying the doping anions. The detection of methanol reached to 10 ppm. They found three response patterns depending on the doping anions.

Selampinar *et al.* (1995) used an electrochemical polymerization to synthesize polypyrrole-polyamide composite (Ppy-PA). The synthesized polymer was exposed to  $\text{NH}_3$  and  $\text{CO}_2$  and consequently measured the resistivity response. The result showed that the gas sensitivity of Ppy-PA to  $\text{NH}_3$  and  $\text{CO}_2$  was greater than those of the pristine polymer in terms of both temporal and reversible responses. Moreover by comparing FTIR, SEM, a solubility study and a pyrolysis experiment between the electrochemical synthesized polymer and the mechanical blending polymer, the electrochemical route yielded graft conducting polymers.

Brie *et al.* [1996] studied effect of initial conductivity and doping anions on gas sensitivity of conducting Ppy films to ammonia. They found that the response of  $\text{TsO}^-$  doped Ppy films to ammonia was different from that of Ppy doped with  $\text{ClO}_4^-$ . The sensitivity to  $\text{NH}_3$  was higher for the Ppy films with a lower initial conductivity. The responses of the Ppy films were identical for a long time interval. The response of Ppy to  $\text{NH}_3$  was explained by Yadong *et al.* in 2000. They stated that the electrons of  $\text{NH}_3$  acted as the donor to the P- semiconductor Ppy with the consequence of reducing of the number of holes in Ppy and increasing the resistivity of polypyrrole.

In 2000, Prisanaroon *et al.* reported Ppy films doped with DBSA used to detect small amounts of  $\text{SO}_2$  in  $\text{SO}_2\text{-N}_2$  mixtures. The short time conductivity response of the conductive films was improved at higher doping levels or by

exposures to higher SO<sub>2</sub> concentrations. The gas sensitivity of a film of a given doping level, as measured by  $\Delta\sigma_{dc}$ , increased with SO<sub>2</sub> concentration. However, for a given SO<sub>2</sub> concentration, the gas sensitivity of the conductive films depended on the doping level. Below a critical doping level, the gas sensitivity was independent of doping level. Above the critical doping level, the gas sensitivity rised sharply to a maximum and then slightly declined as the dopant concentration was increased. The results were interpreted in terms of the changes in the conductive film morphology from three-dimensional random coils to rod-like fibrillar structures.

In 2003, Ruangchuay *et al.* used Ppy doped with seven dopant anions, at 1/12 D/M ratio to detect acetone vapor. They found that the specific electrical conductivity change depended exponentially on the type of dopant, doping level. It also depended linearly on the proportion of bipolaron and of the order of aggregation of Ppy. However it depended inversely on the proportion the imine-like defect. The interaction between Ppy and acetone vapor was investigated by SEM and XRD. The swelling, the hydrogen-bonding formation, and the reduction of charge carriers played an important role in the change of specific conductivity.

## 2.5 The Interaction Between Gas and Zeolite

Ferrari *et al.* (1997) studied the interaction between CO and alkali cations, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>, in the zeolite frameworks by using the density function model cluster calculation. They demonstrated that the interaction between CO and alkali ion was an electrostatic interaction. The O atom of CO bounded to the cation caused the red shift of the CO stretching in contrast to the bounded C atom that caused the blue shift of the CO stretching.

Li *et al.* (1999) conducted FTIR experiments and simultaneously use an ab initio calculation to observe the interaction between CO an alkali earth cation. The computational results reproduced the observed trends in the experimental vibrational frequencies and confirmed that interaction was the electrostatic interaction.

In 2000, Yamasaki *et al.* studied the absorption behavior of CH<sub>4</sub> and CO in pores of  $\Omega$ -zeolite by using FT-IR and an absorption measurement. CO was preferentially adsorbed in the small pores, the 8-membered oxygen ring. CH<sub>3</sub> was

absorbed in the smaller pores when the temperature was higher than 250 K. The ad molecule in the smaller pore suffered a strong van der Waals interaction. The admolecule in the larger pores experienced a strong electric field,  $6.3 \times 10^9$  V/m..

Piti *et al.* (2001) studied the absorption of NO and CO onto Cu-ZSM by using an ab initio embedded cluster methodology at the B3LYP level of theory. For absorption of CO, the calculated binding energy was 32 kcal/mol which was nearly the same as the experimental data obtained between 29 to 32 kcal/mol. For the absorption of NO, the calculated binding energy was 22 kcal/mol which was much smaller than the experimental value.