

CHAPTER II LITERATURE SURVEY

2.1 Synthesis and Doping process.

In 1994, Xia et al. studied the large difference in conductivity of PANI that were prepared from different routes by using UV/Vis/near-IR to examine the changes in conformation and the conjugation length. They prepared thin films of PANI/HCSA spun from chloroform or NMP that had a random coil conformation and a short conjugation length. Those films spun from m-cresol had an expanded coil-like conformation and a long conjugation length. The coil like conformation could be irreversibly converted to expanded coil-like conformation by exposure to m-cresol vapor at room temperature. They concluded that the differences in the conformation and the conjugation length brought about the large difference in conductivity observed.

In 1995, Show-An Chen et al. reported that the ionic salt such as LiClO_4 , LiBF_4 , LiBF_6 and $\text{Zn}(\text{ClO}_4)$, could be used to dope PANI by mixing with a common solvent, 1-methyl-2-pyrrolidone, and then casting the solution to obtain films. The structure and properties of ionic salt-doped-PANI were investigated by using UV-Visible, IR, XPS Spectroscopic techniques, dynamic mechanical analysis, Scanning Electron Microscopy and conductivity measurement. They found that the PANI was doped via pseudoprotonation of the imine nitrogen by the metal cations. The LiBF_4 -doped PANI film retained a conductivity at the level of 10^{-2} S/cm in the temperature range 25-140°C. And it decayed to 10^{-3} S/cm as temperature increased to 175°C, resulting from the increase in ring distortion in the PANI subchains due to the glass transition.

In 1995, Levon et al. doped a polyaniline by introducing the dopant molecules into the polymer backbone without the use of auxiliary solvent. Complex formation in the solid phase occurred at elevated temperature and

resulted in the formation of a soluble and processable conducting complex. In this study, they observed for the first time the effect of doping ratio by on the complexation by using a calorimetric method. The improved processing condition might be the reason for the formation of the layered structure possessing strongly anisotropic characteristics.

In 1997, Joo et al. compared the temperature dependence of the DC conductivity for doped polyaniline pellet samples prepared with various dopants in organic solvents and found that the localization length of the systems sensitively changed in polar solvents. They also reported that both the dielectric screening by the polar solvent and hydrogen bonds between the polymer backbone, the dopant, and the solvent played an important role in controlling the interchain interaction and the conductivity. Furthermore, they confirmed that the DC conductivity increased as the crystallinity increased.

In 1997, Geng et al. doped PANI powders and films with macromolecular acids prepared by solution blending of PANI and the corresponding acids. They found that the conductivity of the doped PANI depended on the solution concentration, structure of the macromolecular acid used and the preparation method. For instances, when using sulfonated polystyrene (SPS), the conductivity of doped PANI increased gradually with increasing sulfonated degree (SD) at the SD below 60 mole %, when SD was over 60 mole % the conductivity was almost constant. Higher conductivity was obtained when PANI was doped with sulfonated PEEK (SPEEK) and PPO (SPPO) rather than with SPS, if comparable SD and concentration were used. This was due to a more expanded conformation of main chain of SPPO and SPEEK in NMP/DMF solutions.

In 1997, Shimizu et al. investigated a new approach to synthesize polyaniline sulfonic acid, a self-doped conducting polymer. This polymer was developed for a variety of applications including a coated film for resist and

conductive button layers of multi-level resist by selecting 2-methoxy aniline-5-sulfonic acid as monomer.

In 1997, Tsutsumi et al. prepared polyaniline-poly(*p*-styrenesulfonic acid) (PSS) composite by thermal post-polymerization of PANI-*p*-styrenesulfonic acid (SSA) composite. A PANI-SSA composite was prepared by mixing PANI/*N*-methyl-2-pyrrolidone solution with SSA aqueous solution and casting onto an ITO glass-plate. The cast film was converted to PANI-PSS film by heating at 100°C for 3 h. The PANI-PSS modified ITO electrode showed electrochemical responses based on the redox reaction of PANI-PSS composite in the organic electrolyte solution. This composite was a cation-doping polymer composite. It was also modified on a porous carbon material (RVC). Its electrochemical behavior was similar to the PANI-PSS modified RVC electrode.

In 1998, Sertova et al. showed that PVC could be used as a solid solvent for PANI(EB)-composite film. The protonation of EB occurred through HCl diffusion within the polymer chain in the PANI(EB)/PVC composite. However, the electrical conductivity of the blend was undetectable, even after a long exposure time. Additionally, they found that NMP was not a good solvent for preparation in the solid state in such compositions in which PVC was included because in this case PVC could not play the role of HCl protogenerator.

In 1999, Liu et al. found a novel strategy for the enzymatic synthesis of a water-soluble, conducting polymer (PANI)/Sulfonated polystyrene (SPS) complex. They used enzyme horseradish peroxidase (HRP) to polymerize aniline in the presence of polyanionic template, sulfonated polystyrene. The reaction was carried out in a 4.3 pH buffered aqueous solution, with a stoichiometric amount of hydrogen peroxide and a catalytic amount of enzyme. The reversible redox activity of the polyaniline displayed a unique hysteresis loop with pH change. Cyclic voltammetry study showed only one

set of redox peaks over the potential range of -0.2 to 1.2 V, which suggested that the PANI/SPS complex was oxidatively more stable. The conductivity of the complex was found to increase with the molar ratio of PANI to SPS. Conductivity of pure complex was about 0.005 S/cm and might be increased to 0.15 S/cm after additional doping by an exposure to HCl vapor. This enzymatic approach offered unsurpassed ease of synthesis, processability, stability and environmental compatibility.

In 2000, Hue et al. reported that the novel n-doped PANI, which were soluble in dimethyl sulfoxide (DMSO), could be obtained by a reaction of the emeraldine base type polyaniline with strong reductants, KH or NaH. It was the first n-doped PANI so far. At room temperature, it had a conductivity of 10^{-1} - 10^{-2} S/cm and a spin density of 3.4×10^{20} (KH) and 4.3×10^{19} spin/g (NaH) comparable to that of the self-acid-doped polyaniline and magnitude higher than those of acid-doped PANI. It could be undoped by adding deionized water into the solution when exposed to air, the conductivity decreased rapidly by 6 orders of magnitude within 1 minute due to undoping by moisture.

In 2000, Luzny et al. presented the result of the film samples of PANI/CSA system, prepared under various conditions. They showed that the conductivity of the samples strongly depended on both the degree of crystallinity and the degree of order of the dopant anions. This ordering could be described quantitatively by the relative intensity of properly selected diffraction reflections. In addition, they investigated the anisotropy of the films by a comparison of the diffraction patterns obtained in a transmission and reflection geometry of diffraction.

In 2000, Young et al. investigated the annealing effects of a dilute polyaniline solution on chemical and physical properties. By contrast to the previously reported reductive reaction, they concluded that the annealing of dilute EB/NMP solution resulted in cross-linking. This was indicated by the decrease of the mutual diffusion coefficient at infinite dilution (D_0) and the

increase in the apparent hydrodynamic radius (R_h) of EB with the annealing temperature evidenced by the DLS and the increase of the cyclic-N portion from ESCA results. The annealing also produced a polyelectrolyte chain as evidenced by FTIR and DLS data.

In 2000, Jelders et al. synthesized the conducting Polyaniline/Calixarene Salt and its property was observed. They reported that emeraldine base could be doped with the sulfonated calixarene host species, calix[4]-*p*- tetrasulfonic acid and calix[6]-*p*-hexasulfonic acid in water or DMSO solvents, yielding novel colloidal conducting emeraldine salt PANI calix[4]SO₃H(3) and PANI calix[6]SO₃H(4). The particle sizes of colloidal 3 and 4 were 517 and 279 nm, respectively, and conductivities of the pressed dried pellets of the 3 and 4 were 3.2×10^{-4} and 2.9×10^{-4} S/cm, respectively. In addition, the colloidal dispersions was electroactive and could also be chemically oxidized and reduced. Chemical dedoping with NaOH and redoping with HCl of 3 and 4 were also possible, and the results showed that the 3 and 4 obtained enhanced stability, due to their counterions, toward alkaline dedoping.

In 2000, Thomas et al. studied new solution processing systems with the goal to obtain highly conductive polyaniline films with good mechanical properties and its conducting blends with poly(methyl methacrylate). A new dopant, namely, 1,2-benedicarboxylic acid,4-sulfo,1,2-di(2-ethylhexyl)ester (DEHESPA), was studied as a protonating agent. It was found that the use of this dopant together with dichloroacetic acid (DCAA) or difluorochloroacetic acid (DFCAA) as solvents leads to films showing conductivities of 180 and 100 S/cm, respectively. Films cast from DCAA were metallic in character down to 200 K. Since the protonation agent used exhibited doping as well as plasticizing properties, the resulting polyaniline film showed excellent flexibility and much lower glass-transition temperature, (280K). Moreover, the same processing system could be used for the fabrication of polyaniline-poly

(methyl methacrylate) blends with low percolation threshold (much below 1 wt % of PANI).

2.2 Sensor Applications.

In 1995, Hidaka et al. reported that electrochemically synthesized choline oxidase polyaniline membranes exhibited permeability to O_2 and H_2O_2 as confirmed by amperometric measurements. Choline oxidase entrapped polyaniline membrane coated on a Pt electrode was applicable as a biosensor for choline by the amperometric measurement of O_2 reducing current with a time response of less than 10s with a dynamic range of 1 M to 0.1 M. Choline and H_2O_2 oxidizing current with time response of less than 20s with a dynamic range of 0.2 mM to 5 mM.

In 1996, Kukla et al. proposed a new type of ammonia sensor with polyaniline as the sensitive element. Such sensors were characterized by high sensitivity, a wide range of measured concentrations (1-2000 ppm) and high stability of electrical parameters. Additionally, the use of polyaniline ensured high chemical stability of sensors in oxidizing ambients. A sensor design based on a silicon chip custom-packed into a linear plastic case was presented. The chip was provided with a system of heaters and thermometers to check the temperature regime of sensor operation. They studied $I-V$ curves, temperature, concentration and kinetic characteristics of the sensors, as well as their aging. The possibility for the thermoregeneration of the sensor parameters after a long-term functioning in an ammonia ambient was emphasized.

In 1996, Sangodkar et al. reported the fabrication of polyaniline-based microsensor arrays for detection of glucose, urea, and triglycerides. Microelectronics technology has been used to produce gold interdigitated microelectrodes on oxidized silicon wafers. Polymer deposition and enzymes immobilization have been done electrochemically. Electrochemical potential

control was used to direct enzyme immobilization onto chosen microelectrodes and to prevent other microelectrodes from contacting with the enzyme solution. This enabled the immobilization of three different enzymes on three closely spaced microelectrodes, resulting in a sensor array which could analyze a sample containing a mixture of glucose, urea, and triolein in a single measurement using a few microliters of the sample. This strategy was quite general and could be extended to other enzyme-substrate systems to eventually produce an 'electronic tongue'.

In 1996, Mu and Xue. proposed that a glucose biosensor could be prepared by both adsorption and electrochemical doping on/in a polyaniline film. It had a high operational stability and long storage stability of 36 months.

In 1997, Laranjeira et al. developed a simple conductimetric system to detect ammonia concentration in fertilizer samples using PANI films. Its conductivity decreased when exposed to an ammonia gas and the response can be related to the ammonia concentration. Its advantages were low operational cost, simplicity of operation, good sensitivity, good precision and very accuracy.

In 1997, Dhawan et al. illustrated that the leaching of the polaronic sites in the doped PANI grafted surface on exposure to aqueous NH_3 led to a characteristic resistance change in the polymer. The surface resistance of the doped PANI changed from 10^2 to 10^{10} ohm when exposed to NH_3 .

In 1997, Yoon et al. investigated the electrical transport properties of phosphoric acid doped polyaniline by the measurements of low temperature conductivity and thermopower. Samples were prepared by chemical polymerization of aniline in aqueous solution of phosphoric acid at various ratios of acid to aniline (Z). The conductivity at room temperature increased from 3 S/cm to 40 S/cm, and the thermopower increased from $+0.2 \mu\text{V/K}$ to $+7.6 \mu\text{V/K}$, as the Z ratio varied from 1 to 6. The low temperature conductivity followed variable range hopping (VRH) temperature dependence,

$\ln \sigma \propto 1(T_0/T)^x$, where VRH exponent systematically changes from $x = 1/2$ to $1/4$. The thermopower changed from U-shape to linear temperature dependence as the Z ratio increased. The systematic variation of transport data was analyzed by considering heterogeneous contributions from metallic transport and VRH process in a disorderd polymeric system.

In 1997, Lukachova et al. proposed immobilization of a glucose oxidase (GOD) into Nafion membranes. Since Nafion was deposited from its real solution without excessive dissolving in water, the resulting membranes were more uniform and stable. The remaining activity of glucose oxidase, after a 30-min exposure to such solutions under optimal conditions, was up to 100%. The stability of the GOD in these suspensions was higher than in aqueous solution. Potentiometric polyaniline-based biosensor made according to the proposed method of enzyme showed a several times increased response as compared with enzyme electrodes developed in the traditional way using excessive dilution of Nafion with water. The remaining activity of the enzyme electrode made by GOD immobilization from concentrated organic solvent was 95-100% after several drying-washing cycles.

In 1997, Centonze et al. found that glucose in soft drinks, fruit juices, and milk was determined by an interference-free amperometric biosensor coupled with microdialysis fibre samples. The biosensor was based on glucose oxidase (Gox) immobilized on a platinum electrode by an electroproduced bilayer of overoxidized polypyrrole (Pt/Ppyox, Gox, PPYox). It showed a linear response up to 500mM and was not sensitive to pH variation in the range of 2-10. They also investigated the influence of flow rate on biosensor response. Glucose response of the device in continuous and discontinuous flow injection experiments showed good repeatability and sensitivity.

In 1998, Cho et al. developed a new procedure for urea determination. By cross-linking urease onto a polyaniline-Nafion composite electrode which sensed the ammonium ions, a very sensitive urea biosensor was developed.

The effects of applied potential, pH of buffer solutions, flow rate of carrier, and possible interferences on the response of urea biosensor were studied. With the developed urea biosensor, a detection limit as low as 0.5 μM and a response time as short as 40 s were obtained in flow injection analysis system. A relative standard deviation of 2.2 % (n=15) was obtained for the successive analysis of a 0.03 mM standard urea solution. Applicability of the urea biosensor for urea analysis was demonstrated by the analysis of NIST standard reference material and urine samples.

In 2000, Min et al. showed that porous silicon could be used as a chemical sensor for detecting extremely low concentration of ethanol solutions. Fabry-Perot fringes measured from the porous silicon layer in ethanol solution were changed as the concentration of the solution was varied. Standard deviation of the difference between the fringe patterns obtained in ethanol solutions and deionized water showed an almost linear relationship to the logarithm of the ethanol molar concentration in the range between 1×10^{-5} and 1×10^{-14} M.

In 2000, Stella et al. presented the selection and test of an array of conducting polymer sensors with extra-virgin olive oil. Different sensors produced by both electrochemical and chemical techniques were initially exposed to a set of pure substances present in the headspace of extra-virgin olive oil and meaningful for the evaluation of its overall organoleptic characteristic. Two different experiment set-ups and protocols for olive oil sampling were tested and compared, providing evidence on the best procedure needed to handle this foodstuff and on the possibility of using a dedicated sensing system of practical purposes in the olive oil industry. Three different extra-virgin Italian types of olive oil could be easily distinguished with an array of four sensors and it was also possible to detect changes in the aromatic content of the headspace after handling of the samples. Different samples of the same oil showed reproducible response.

In 2000, Prissanaroon et al. investigated the effects of using dodecylbenzene sulfonic acid as a dopant on electrical conductivity of Ppy films in N₂ atm and SO₂-N₂ mixtures. They found that the short-time conductivity response of the conductive films could be improved by higher doping level or by exposure to higher SO₂ concentrations. The gas sensitivity of 2 films of a given doping level increased with SO₂ concentration. For a given SO₂ concentration, the gas sensitivity of the conductive films depended on the doping level. Below a critical doping level, the gas sensitivity was independent of the doping level. It could be interpreted in terms of the change in conductive film morphology from random coils to rod-like fibrillar structure.