

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Sensitivity Improvement of PPy-Based Sensor for Acetone Vapor

Among seven dopants used in this work, α -naphthalene sulfonate and β -naphthalene sulfonate are the most suitable ones for PPy by an *in-situ* doped polymerization process. They provide PPy with the best mechanical, chemical and electrical properties. As increasing amount of α -naphthalene sulfonate dopant during polymerization, the α -naphthalene sulfonate-doped PPy (PPy/A) has better electrical properties. The maximum doping level in terms of N^+/N is 0.24 - 0.27. The dopant to monomer molar ratio (D/M ratio) giving PPy/A with the highest specific conductivity and stability is 1/12. This D/M ratio corresponds to the ratio between the dopant and the yielded PPy of about 1/3, which is close to the maximum N^+/N obtained. Beyond the D/M ratio of 1/12, the dopant molecules become overcrowded during polymerization. This hinders the electron conduction mechanism.

The electrical sensitivity to acetone vapor of conductive PPys was modified by utilizing various types of dopant and various dopant concentrations during polymerization. The dopants which provide PPy with higher specific conductivity, higher order aggregation, higher proportions of charge carrier species, especially bipolaron ($-NH^{+-}$), and lower proportion of imine-like nitrogen defect ($=N-$) are the effective ones in improving the sensitivity to the acetone vapor. The PPy/A and the β -naphthalene sulfonate-doped PPy (PPy/B) are the most promising candidates amongst PPys investigated as polymeric sensor materials used in detecting acetone vapor. The optimum D/M ratios for this application are 1/24 – 1/6.

As investigated by ESEM and XRD, acetone swelled PPy. Its molecules diffused into the intersegmental spaces in the PPy matrices, which were previously separated by the dopant molecules. They also destroyed the dispersing forces between aromatic pyrrole rings, as evidenced by XRD. Acetone molecules chemically absorbed onto a PPy matrix *via* a hydrogen-bonding, as seen by TGA and FT-IR. These interactions hindered the electron jumping and hence decreased the

specific conductivity of PPy. Moreover, the presence of water molecules in the form of moisture content in PPy matrix seemed to suppress the response to acetone by reducing the accessible active sites (neutral and charged $-NH-$). The changes in visible spectra of PPy/B during an acetone exposure indicated the reduction of charge carrier species, especially bipolaron. This explains the best sensitivity of PPy/A and PPy/B which have relatively high proportion of charge carries species, especially bipolaron in PPy/A.

7.2 Selectivity Improvement of PPy-Based Sensor for Vapors of Flammable Chemicals Vapors in Lacquer

Blends of PPy/A and common insulating polymers have been successfully prepared as highly selective sensors. The blends of PPy/A and PS, ABS, or PMMA from solution mixing showed a significant improvement in sensitivity and temporal response toward acetone and toluene, primarily due to the swelling effect. Moreover, the response toward water, a serious interference problem for on-line sensors, was successfully diminished. The PMMA-coated PPy/A is an ideal water-insensitive sensing material; however, it had an appreciable induction period and poorly reproducible responses toward the target chemicals.

The film of PPy/ α -NS⁻/PMMA blend cast from solution of toluene was further studied as the sensing material for acetone vapor in lacquer in order to improve the degree of selectivity over both acetic acid and moisture. The blend composition was fixed at 1.0, 2.0, 3.0, and 4.0. Compared to the selectivity ratio of acetone/acetic acid response of pure PPy, which was 0.7, the selectivity ratio of PPy/ α -NS⁻/PMMA blend with PMMA/PPy weight ratio of 3.0 was about 3.6 times higher. However, this material could be used only once. This selectivity ratio was found to be unaffected by a change in humidity except at very low relative humidity, at about 20%, where the selectivity ratio was enhanced. The possible reason was the loss of water from the film; at low relative humidity, the amount of active sites for acetone increased, but not for acetic acid which prefers protonation at $-N=$ of PPy as revealed by XPS. The time required to reach the equilibrium signal at 20 – 50 %RH

for an acetone exposure was only 8 - 12 min. It was as high as 45 min for an acetic acid exposure due to a lower vapor pressure of the vapor.

7.3 Stability Improvement of PPy-Based Sensor for Vapors of Flammable Chemicals Vapors in Lacquer

For the solution blending results, the film of PPy/ α -NS⁻/PMMA blend not only showed good mechanical properties, but also gave a good stability in electrical signal when exposed to acetone and acetic acid at different values of relative humidity in N₂.

7.4 Surface Degradation of α -Naphthalene Sulfonate Doped Polypyrrole during XPS Characterization

The heat-induced surface degradation of conductive PPy sample during XPS experiment was studied. When the liquid nitrogen cooling kit was utilized, reproducible XPS spectra of the non-aging chemically synthesized PPy/A was obtained under the high-power X-ray source with accumulated X-ray exposure time up to 1050 min. Beyond this time, further X-ray exposure can result in further deprotonation of polaron charge carrier species in PPy and the desulfonation of α -naphthalene sulfonate dopant. The gradual formation of sulfur-containing species was observed. Without utilization of a cooling kit in the XPS instrument, this degradation became even more severe, indicating that these degradations were mainly induced by heat from the X-ray source.

7.5 Recommendations for Future Work

The gas sensing experiment in this work has been carried out in N_2 atmosphere. The preliminary result when using synthetic air as a carrier gas, composing of O_2 and N_2 , in stead of N_2 , was done but not reported here. Even though our results showed no difference between these two carrier gases, the effect of O_2 in synthetic air on the sensing performance of PPy-based gas sensor is interesting for further investigation, especially, for a prolonged exposure and at a high temperature. Under the presence of O_2 , interactions between PPy and chemical vapors are expected to be more complicated, especially at high temperature. However, if the results can be understood, a possibility of having an inexpensive and portable online-sensor for these flammables chemical seems likely.