**Abstract**

Polypyrrole, an Intrinsically Conductive Polymer (ICP) was obtained through chemical oxidative polymerization of pyrrole and a low temperature sensing device was designed by pelletizing Ppy/Piezoceramic powder composite with Tin. Raw/Green pellets of Ppy/PZT composite were liquid phase sintered above the solidus temperature of Tin metal ($254^\circ$C) to yield the final sensor. Current-Voltage ($I-V$) characteristics of two such sensor samples were analyzed. Sensor sample with 4 % Tin yielded maximum conductivity of 9.12 S/cm as compared with the sensor sample with 3 % Tin, conductivity dropped to 5 S/cm. Also, almost non-linear trend in the I-V curves was observed due to the environmental factors such as a small temperature range between $0^\circ$C-$110^\circ$C. Characterization of both the sensor samples using SEM confirmed that the sensor with higher Tin content behaved as a better sensor than the sensor having a lower Tin content.

**Keywords:** Conducting Polymers, Polypyrrole, PZT, Ppy/PZT Temperature Sensor, Sensor Design

**1. Introduction**

Since they were discovered by H. Shirakawa and co-workers in 1977, conducting or conjugated polymers such as polypyrrole have attracted widespread attention worldwide among chemists and material scientists alike. More accurately known as Intrinsically Conducting Polymers (ICP's), these are organic polymers that conduct electricity. In an ideal situation, polymers possessing a single, continuous band of overlapping valence and conduction bands should conduct and so should metals, without the need for doping. High electrical conductivity is displayed by the polymers, which have overlapping bands. Owing to this ability, these classes of materials are nowadays widely used in electronic devices since conducting polymers are cost effective, mechanically flexible, easily fabricated and more tractable than inorganic semiconducting polymers.

Polypyrrole or polypyrrole black, as it is called; it can be synthesized by chemical oxidative or electrochemical polymerization techniques. What makes polypyrrole so unique is its extremely high conductivity which can go as high as 1000-2000 S/cm in the pure polymer, excellent air and thermal stability and excellent corrosion resistance.

Micro-emulsion polymerization and inverse emulsion polymerization techniques are usually employed to prepare polyaniline and polypyrrole. In this, solution of a hydrophilic monomer is emulsified in a non-polar organic solvent and polymerization is initiated with an oil-soluble initiator.

An attempt has been made herein to synthesize polypyrrole employing inverse emulsion polymerization technique using Lead Zirconate Titanate (PZT) piezoceramic powder as a dopant, thereby synthesizing a Ppy/PZT composite. However, the principal difficulty in the practical application of polypyrrole is its poor processability and mechanical properties, which restricts its practical applications. To counteract this difficulty, pellets of Ppy/PZT composite were generated using the traditional powder
compaction technique in a hydraulic pellet press with Tin (Sn) metal powder in varying proportions to produce “green” or raw pellets which were then liquid phase sintered in a Therelek furnace at 254°C, i.e. above the solidus temperature of Tin, to produce the final device. Tin metal acted as an intermediate binding liquid phase between Ppy/PZT composite which was subsequently confirmed during the SEM studies. A comparative was drawn between two such devices with varying percentages of Tin metal powder to elucidate which device worked as a better temperature sensor.

There are numerous advantages of liquid phase sintering such as very quick densification times as compared to solid phase sintering and the particle densification depends upon the intermediate binding liquid phase.

2. Experimental Procedure

2.1 Polymerization Technique

2.1.1 Preparation of Polypyrrole Saltusing Lead Zirconate Titanate (PZT) Piezoceramic Powder as a Dopant

A mixture of PZT dopant (6.0g) and water (25ml) was taken in a 250 ml conical flask. Pyrrole monomer (1.2ml, 1.16g) dispersed in water (35ml) was added to the above mixture and constantly stirred at 20°C. Sodium lauryl sulfate surfactant (1.0g) dispersed in water (30ml) and Potassium persulfate initiator (3.0g) dispersed in Chloroform (20ml) were added drop wise to the stirring reaction mixture. The reaction mixture was allowed to stir constantly for one hour duration, after which it was poured in acetone to precipitate the grey colored polymer. The polymer was washed with water, dried in an oven at 100°C, and weighed until a constant weight was obtained.

2.1.2 Design and Development of Ppy/PZT Temperature Sensor

Premeasured Ppy/PZT composite was blended with varying proportions of Tin (Sn) metal powder; since two devices with Ppy/PZT composites were formulated, Tin metal powder was taken in varying proportions (percentages), i.e. 3 % and 4 % with respect to 100g of pellets of Ppy/PZT composites. These blends/composites of Ppy/PZT/Sn were then compacted in hydraulic KBr pellet press and a pressure of 6-7 tons was applied for 2-3 minutes to yield a “green” or a raw pellet, which was subsequently liquid phase sintered at 254°C (i.e. above the solidus temperature of Tin metal) for one hour duration. Tin metal powder was expected to act like an intermediate liquid phase between the dispersed Ppy and PZT. I-V characteristics of such doped pellets were studied and a comparative was drawn which device performed as a better temperature sensor, based upon the temperature dependence of the doped pellets.

3. Results and Discussion

Table 1 summarizes various raw materials used for the design and development of Ppy/PZT sensor. Raw materials used were with respect to 100 g of pellets which were formulated.

Two sensor devices were formulated; one with 4.0 % Tin (Sn) and the other with 3.0 % Sn. Figure 1 and Figure 2 depicts these curves for 4.0 % Sn and 3.0 % Sn respectively. I-V curves were studied in the temperature range of 273 K to 383 K and were found to be almost non-linear in their characteristic, mainly due to the small temperature range studied, i.e. from 273 K-383 K yet confirming the electrical charge distribution through the polymer backbone chain. It was seen that the electrical conductivity obtained in the sensor device with 4.0 % Sn was 9.1 S/cm while the electrical conductivity in the sensor device with 3.0 % Sn was 5.0 S/cm, i.e. almost more than double as evident from Figure 3 and Figure 4. This sudden and sharp increase in conductivity was due to two reasons; first, since the concentration of tin metal powder is varied by almost 1 % in the sensor devices, effective liquid phase sintering could have occurred leading to the elimination of pores and effective grain growth and subsequent particle densification in the Tin liquid matrix; and second reason is formation of a full conducting path for the flow of current beyond a point called percolation threshold for a certain amount of the polymer, which is a critical point at which the particles

| Materials     | Percentage | Amount | Particle Size |
|---------------|------------|--------|---------------|
| Polypyrrole   | 60 %       | 60 g   | 4420 nm       |
| PZT           | 40 %       | 40 g   | 950 nm        |
| Tin (Sn)      | From 3.0 % to 4.0 % | Variable | Market Grade |
of the polymer exist as giant clusters which facilitate the flow of current and conductivity arises. Below this percolation threshold there is no significant conductivity since particles do not form clusters. This is evident from Figure 5 which depicts the SEM image of a sensor having 4.0 % Tin. It is seen clearly in the figure that there is distribution of liquid Sn between spherical particles of Ppy/PZT with an intermediate liquid film. However, it is evident from Figure 6, which is the SEM image of the sensor having 3.0 % Tin, intermediate liquid film is visible but there is no cluster formation. Therefore, it can be said that the sensor having 4.0 % Tin concentration shows improved texture as compared to the sensor having 3 % Tin.
4. Conclusions

A low temperature Polypyrrole/PZT (Ppy/PZT) sensor was successfully developed which operated at a temperature range of 273 K to 383 K. Tin (Sn) metal powder was used as an intermediate binding material during the liquid phase sintering of Ppy/PZT pellets. Almost non-linear I-V curves were obtained and yet a very high conductivity of up to 9.1 S/cm was obtained in a sensor having 4.0 % Tin concentration. It was concluded that the sensor having 4.0 % Tin concentration behaved as a better sensor than with a 3.0 % Tin concentration.

5. References

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