Sensor studies

5.1 Introduction:

According to Jacob Fraden, a sensor is a device that receives a signal orstimulus and responds with an electrical signal. The reason for the output of a sensor tobe limited to electrical signals is related to the present development of signal processing,that is almost exclusively performed using electronic devices.Recently, gas sensing, as a typical application in intelligent systems, is receiving increasing attention in both industry and academia. Gas sensing technology has become more significant becauseof its widespread and common applications in the following areas: (1) industrial production (e.g.,methane detection in mines (2) automotive industry (e.g., detection of polluting gases fromvehicles (3) medical applications (e.g., electronic noses simulating the human olfactory system) (4) indoor air quality supervision (e.g., detection of carbon monoxide) (5) environmental studies (e.g., greenhouse gas monitoring). During the last fifty years, different studies have established various branches of gas sensingtechnology. Among them, the three major areas that receive the most attention are investigation ofdifferent kinds of sensors, research about sensing principles, and fabrication techniques (1-3).

5.2 Types of Sensors

Generally, sensors can be classified into many types based upon the applications,input signal, and conversion mechanism, material used in sensor, production technologiesor sensor characteristics such as cost, accuracy or range.Based on the input signal given to the sensor, the sensors can be classified into sixdifferent types, which are mentioned in the Table 5.1.

Table5.1 Classification of sensors

Type	Detection Properties
Thermal Sensor	Temperature, Specific heat, Heat flow, etc.
Electrical Sensor	Current, Voltage, Resistance, Inductance, etc.
Magnetic Sensor	Magnetic flux density, Magnetic moment, etc.
Optical Sensor	Light intensity, Wavelength, Polarization, etc.
Mechanical Sensor	Length, Acceleration, Flow, Force, Pressure, etc.
Chemical Sensor	Composition, Concentration, pH, etc.

Potential advantages of the smart-sensor concept include:

- lower maintenance
- reduced down time
- higher reliability
- fault tolerant systems
- adaptability for self-calibration and compensation
- lower cost
- lower weight
- fewer interconnections between multiple sensors and control systems
- less complex system architecture.

5.3 Gas Sensors

Gas sensor is a device that can change the concentration of an analyte gas into anelectronic or electrical signal . A gas sensor is a chemical sensor that is operated in the gas phase. It is an important component of devices commonly known as electric nose .A gas sensor must possess at least two functions: (i) to recognize a particular gasand (ii) convert the output into measurable

sensing signals. The gas recognition is carriedout through the surface chemical processes due to gas-solid interactions. Theseinteractions may be in the form of adsorption, or chemical reactions. Most of the gassensors give an electrical output, measuring the change of current or resistance orcapacitance.The given signal can be related to the chemical environment it is exposed to. Theresponse of a gas sensor to a single gas can be described as:

$$x = f_{gas}(c_{gas})$$

where$f_{gas}$is a function (usually non-linear) and c_{gas}, the concentration of the gas. Theresponse is in most cases defined as the difference or ratio between the steady-statesensor response when exposed to the sample gas and the sensor response when exposedto a reference atmosphere (not sample gas). The concentration-response relationship formost gas sensors approximately exhibits either saturated linear behavior, i.e. linear forlow concentrations and saturated for higher concentrations, or logarithmic behavior.Three important parameters when describing the response of a sensor are sensitivity,selectivity and stability. The sensitivity of the sensor towards a specific gas is, thus,defined as

$$\gamma_{gas} = \partial x / \partial c_{gas}$$

The selectivity (E) of a single sensor is usually defined as the ratio of thesensitivity related to the gas concentration to be monitored in the linear region and themaximal sensitivity to all other interfering components. It is given by

$$E = \gamma_{gas} / \gamma_{max\,all\,other\,gases}$$

The stability of the sensor response is defined as the reproducibility of the sensitivity and selectivity as a function of time.Most of the drawbacks of the commonly used gas sensing technologies comefrom their lack of stability. There are other demands to be met when

producing gassensors, such as short response time, good reversibility, low cost, small size and lowpower consumptions.When a sensing material is exposed to gas, then it interacts with the gas, thisinteraction may be by adsorption or desorption, chemical reactions on the surface or thebulk of the material. The interaction changes some physical properties of the sensingmaterial, such as the electrical conductivity or the mass. The change in conductivityis detected by the voltage drop over a series resistor or a change in mass is detected bythe shift in frequency of a resonator. A schematic description of the working principles ofsolid-state gas sensors is depicted in Figure 5.1

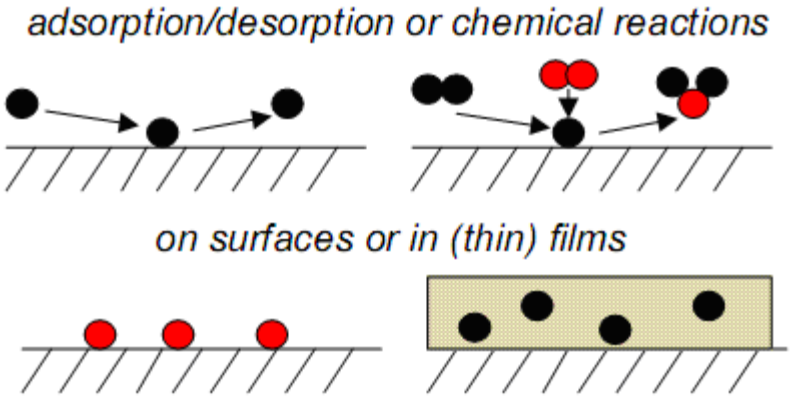

Figure 5.1: Principle of solid-state gas sensors

In the present study, studies are made on LPG sensing.

5.4 Liquefied Petroleum Gas (LPG)

LPG is a mixture of commercial butane and commercial propane having both saturated and unsaturated hydrocarbons.

5.5 PHYSICAL PROPERTIES AND CHARACTERISTICS

DENSITY

LPG at atmospheric pressure and temperature is a gas which is 1.5 to 2.0 times heavier than air. It is readily liquefied under moderate pressures. The density of the liquid is approximately half that of water and ranges from 0.525 to 0.580 @ 15 deg. C. Since LPG vapour is heavier than air, it would normally settle down at ground level/ low lying places.

VAPOUR PRESSURE

The pressure inside a LPG storage vessel/ cylinder will be equal to the vapour pressure corresponding to the temperature of LPG in the storage vessel. The vapour pressure is dependent on temperature as well as on the ratio of mixture of hydrocarbons.

FLAMMABILITY

LPG has an explosive range of 1.8% to 9.5% volume of gas in air. This is considerably narrower than other common gaseous fuels. This gives an indication of hazard of LPG vapour accumulated in low lying area in the eventuality of the leakage or spillage. The auto-ignition temperature of LPG is around 410-580^{0}C and hence it will not ignite on its own at normal temperature.

ODOUR

LPG has only a very faint smell, and consequently, it is necessary to add some odourant, so that any escaping gas can easily be detected. Ethyl Mercaptan is normally used as stenching agent for this purpose.

COLOUR

LPG is colorless both in liquid and vapor phase. During leakage the vaporization of liquid cools the atmosphere and condenses the water vapor contained in them to form a whitish fog which may make it possible to see an escape of LPG.

5.6 Metal Oxide for Sensor Application

The most common sensing materials are metal oxide semiconductors, which provide sensors withseveral advantages such as low cost and high sensitivity. Generally, metal oxides can be classified intotwo types: non-transition and transition. The former (e.g., Al_2O_3) contains elements with only onoxidation state since much more energy is required to form other oxidation states, while the latter(e.g., Fe_2O_3) contains more oxidation states. Therefore, transition-metal oxides could form variousoxidation states on the surface, which is utilized by metal oxide semiconductors as sensing materials,compared to the non-transition ones. More precisely, transition-metal oxides with d_0 and d_{10} electronicconfigurations could be used in gas sensing applications . The d_0 configuration could be found intransition metal oxides (e.g., TiO_2, V_2O_5, WO_3), and d_{10} appears in post-transition-metal oxides (e.g.,SnO_2 and ZnO). Although most common metal oxide semiconductors sensitive to gas concentrationare n-type semiconductors, there are also a few kinds of p-type semiconductors like NiO (usuallydoped with n-type semiconductor like TiO_2) that could be used as gas sensor sensing materials.

Sensors based on metal oxide semiconductors are mainly applied to detect target gases through redox reactions between the target gases and the oxide surface . This process includes two steps (1) redox reactions, during which O^- distributed on the surface of the materials would react with molecules of target gases, leading to an electronic variation of the oxide surface; and then (2) this variation is transduced into an electrical resistance variation of the sensors. The resistance

variation could be detected by measuring the change of capacitance, work function, mass, optical characteristics or reaction energy Metal oxides, such as SnO_2, CuO, Cr_2O_3, V_2O_5, WO_3 and TiO_2, can be utilized to detect combustible, reducing, or oxidizing gases with sensors which are mainly based on the resistance change responses to the target gases . Tin dioxide (SnO_2) isthe commonly used gas sensing material.(4-8)

5.7 Design of Gas sensor setup

The sensors set up consist of rectangular glass box of dimension of 6 x 8 x 18 inches with a total volume of 14,158 cm^3 as shown in figure 5.2. F1, F2, F3 and F4 refer to flow meter used to introduce different test gases into the chamber through the gas balloon, where in test gases mixes [9-10]. The chamber is provided with a heating element to increase the temperature of the sample but in the present study only room temperature measurement has been carried out. The change in electrical resistance was recorded by two probe method using Keithley –6514 electrometer as shown in figure 5.2(a).

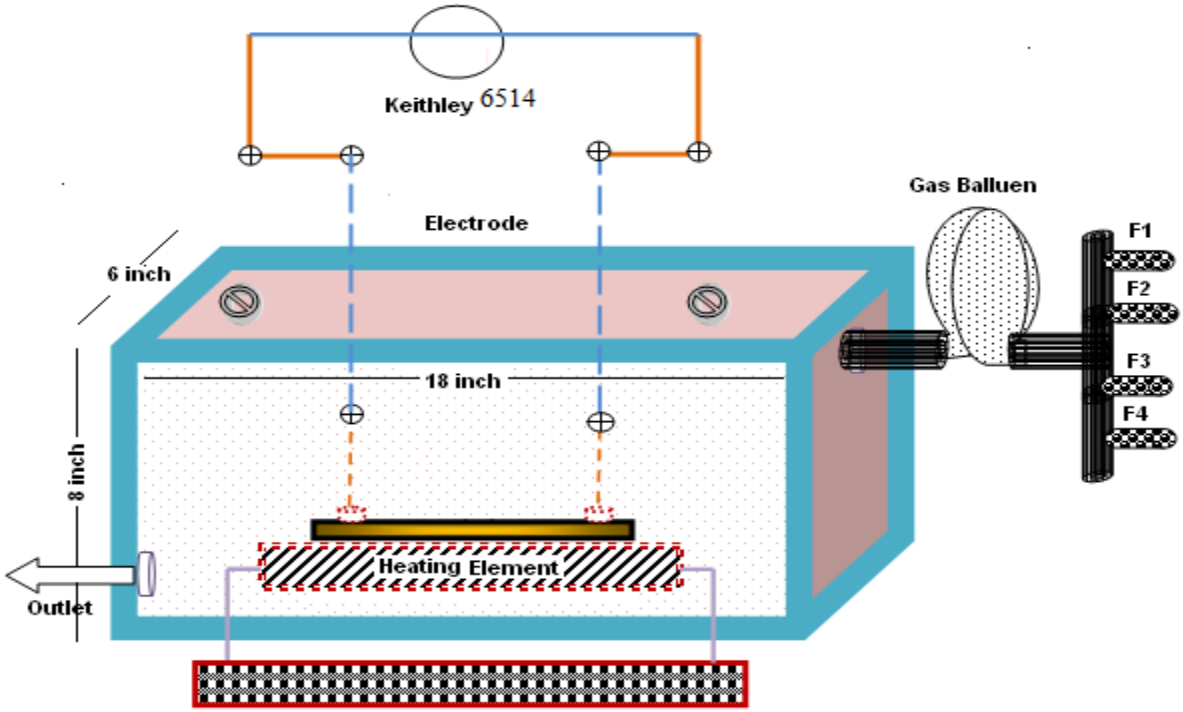

Figure 5.2(a): Block diagram of gas sensor set-up

Figure 5.2(b): Photograph of gas sensor set-up

The present investigation describes the detection of LPG at room temperatureusing polyaniline and metal oxide compositessuch Polyaniline - Nickel Oxide nanocomposites, Polyaniline - Iron Oxide nanocomposites, Polyaniline – Zinc Oxide nanocomposites, Polyaniline - Zinc Ferrite nanocomposites.

5.8 Experimental Technique

The samples in the pellet form were used for LPG sensing behavior ofPolyaniline and Polyaniline - nanocomposites. The planar resistance of the sensor wasrecorded versus time by controlling LPG in a closed glass chamber at room temperature.Controlled LPG at room temperature was introduced steadily into the chamber to increasethe gas concentration inside the chamber. The flow rate of 20 cc / min was adjusted byregulator and gas control valve, the flow

rate is monitored by a flow meter. The planarresistance of the Polyaniline and its composites was recorded versus gas concentration.The block diagram of the gas sensor setup is shown in Figure 5.2 (a) and completephotograph of the setup used for the measurement of electrical resistance versus LPGconcentration is shown in Figure 5.2(b).

5.9 Results and Discussions

5.9.1 Polyaniline

Figure 5.3 shows the change in sensitivity with respect to time for pure Polyaniline at room temperature. It is observed that when the pellets were exposed to a gas, the polymer matrix swells due to absorption of gas. The increase in volume causes an increase in sensitivity whichcauses the disruption of conducting pathways through the sample.

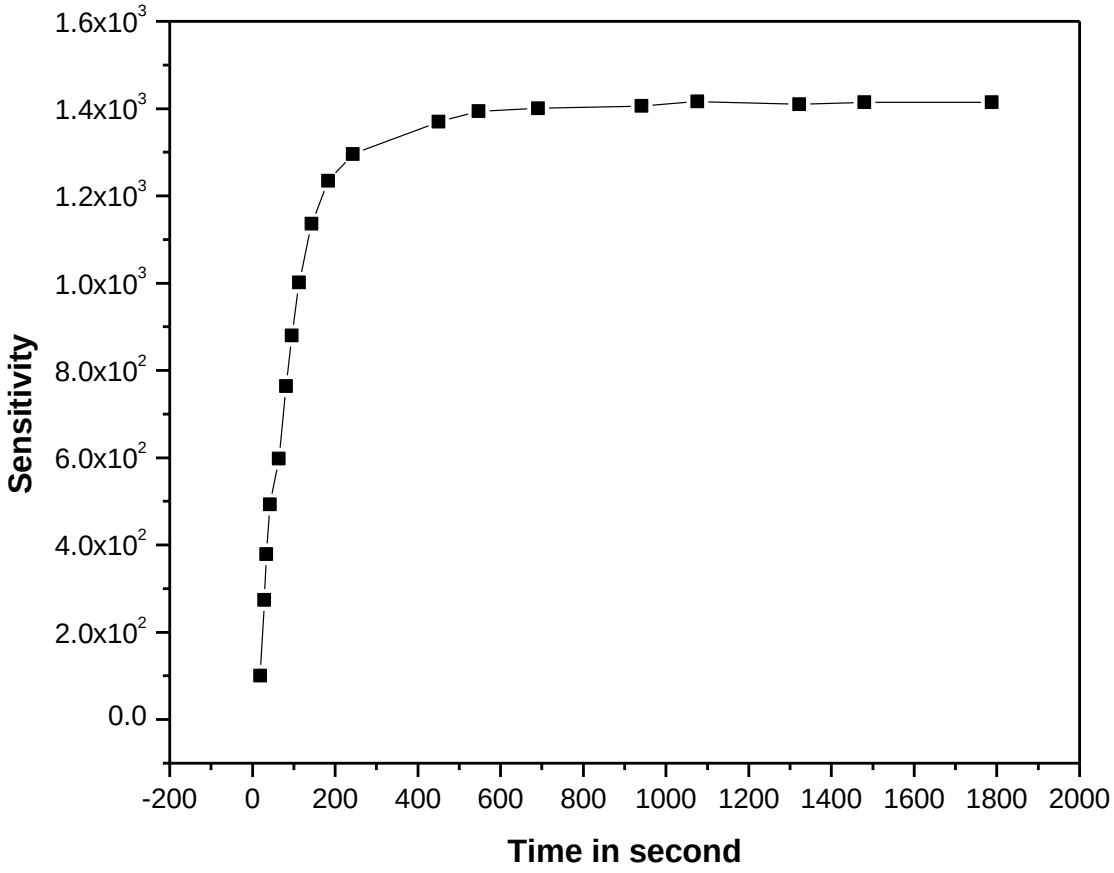

Figure 5.3 shows the change in sensitivity with respect to time for pure Polyaniline

5.9.2 Polyaniline/Nickel Oxide nanocomposites

Figure 5.4 shows sensitivity vs time for Pani/nickel oxide composites.It is observed thatthere is a linear increment in sensitivity and it is also found that it increases up to sometime and decreases after being transferred to clear air. Among all the Pani / nickel oxide nanomposites, 50 wt% are showing maximum Sensitivity when compared to pure pani and other composites and this is due to reaction between the metal oxide and LPG. In the case of pure pani and 10wt% the change in sensitivity is very low due to lower adsorption because of lower surface area. Thisresult clearly

shows that pani / nickel oxide composite is good candidate for LPG sensing with better sensitivity.

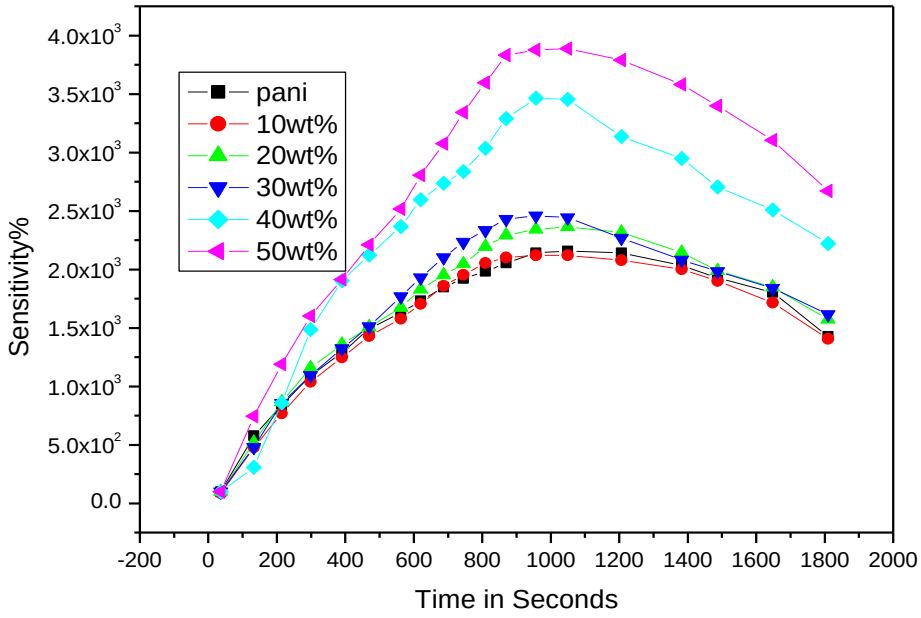

Figure 5.4 shows the variation of sensitivity with time for Polyaniline/Nickel Oxide nanocomposites.

5.9.3 Polyaniline/ Iron Oxide nanocomposites

Figure 5.5shows sensitivityvs time for Polyaniline /Iron Oxide nanocompositesand it is seen that the Pani/iron oxide nanocomposites shows better sensitivity to gas vaporcompared to pure polyaniline. The 50wt% nanocomposites shows higher sensitivity compared to other nanocomposites and this is due to the strong interaction between the Polyanline and iron oxide

nanoparticles. In the case of Pure Polyaniline and 10wt% nanocomposites, sensitivity is very low because of lower surface area.

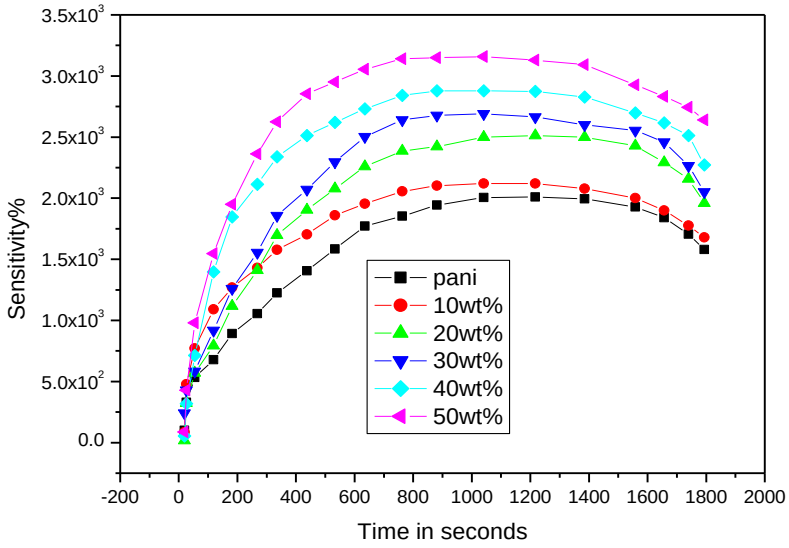

Figure 5.5 shows the variation of sensitivity with time for Polyaniline/ Iron oxide nanocomposites.

5.9.4 Polyaniline/ Zinc Ferrite nanocomposites

Figure 5.6 shows the variation of sensitivity with time for Polyaniline, Polyaniline/Zinc ferrite nanocomposites containing:10wt%, 20wt%, 30wt%, 40wt% 50wt% $ZnFe_2O_4$nanoparticles.Thesensitivity of the nanocomposites was measured at room temperature when exposed to LPG vapors. The Sensitivity of all Polyanilinenanocomposites samples increases with increasing the weight percentage of Zincferrite nanoparticle and the reasons for the increase in sensitivity can be the increase in zinc ferrite adsorption capacity of the contact zone between the charged particles of Polyanilineand Zincferrite nanoparticles. The increasing sensitivity at higher weight percentage may be due to high surface area with possible reaction

sites of the nanocomposites due to adsorption of gas molecules .The gas sensing mechanism of zinc ferrite based LPG sensor is a surface controlled phenomenon i.e., it is based on the surface area of the nanoparticles at which the LPGmolecules adsorbs and reacts with pre-adsorbed oxygen molecules.It is found that the large specific area contributes to the oxygen andLPG adsorption on the surface of the materials, which is responsible for the increase insensitivity of the sensor.

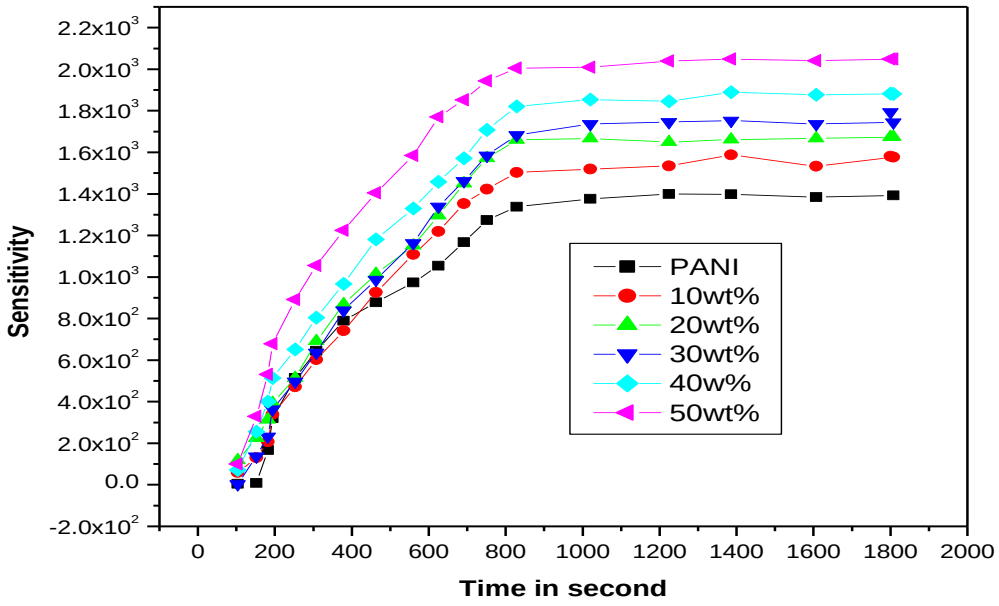

Figure 5.6shows the variation of sensitivity with time for Polyaniline/ Zinc Ferrite nanocomposites

5.9.5 Polyaniline/ Zinc oxide nanocomposites

Figure 5.7 show the change in sensitivity with respect to the time of polyaniline nanocomposites at room temperature. It is observed that when the pellets were exposed to a gas, the polymer matrix swells. The increase in volume causes an decrease in resistance due to this

the conductive pathways through the material are disrupted. When the gas releases, the polymer returns to its original size, restoring the conductive pathways. Thus the sensitivity increases with increase in the concentration of the gas. Among all the PANI / ZnO composites 30 wt% shows maximum change in sensitivity when compared to pure PANI and other composites [11-14].

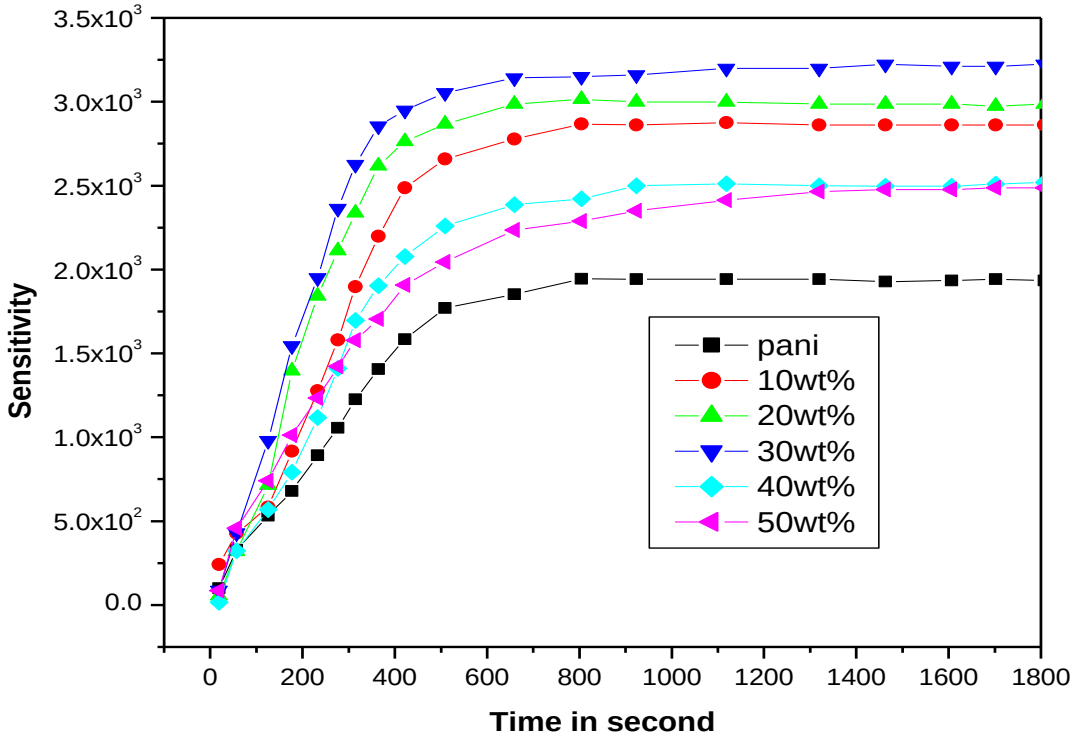

Figure 5.7 shows the variation of sensitivity with time for Polyaniline/ Zinc Oxide nanocomposites

Gas sensing mechanism

The gas sensing mechanism in polyaniline – ZnO composites is expected mainly because of two reasons. First the trapping of LPG molecules in between the polyaniline – ZnO nanocomposites islands by electrostatic forces and second is a surface controlled phenomenon

i.e., it is based on the change in surface resistance of the nanocomposites at which the LPG adsorb and reacts with pre-adsorbed oxygen molecules [15, 16]. The polyaniline – ZnO composites pellet is more porous due to the distribution ZnOparticles in the mesoporous structure (as observed from SEM). Therefore, the oxygen chemisorptions centers viz., oxygen vacancies, localized donor and acceptor states and other defects are formed on the surface during synthesis. These centers are filled by adsorbing oxygen from atmospheric air. When the composites pellet is placed inside the gas sensing setup, after some time equilibrium is established between oxygen adsorbed at the surface of sensing element and atmospheric oxygen through the chemisorptions at room temperature. The stabilized resistance at this state is known as resistance in the presence of air (R_a). The electron transfer from the conduction band to the chemisorbed oxygen results in the decrease of electron concentration at the pellet surface [17]. As a consequence, a decrease in the resistance of the pellet is observed. In LPG, the reducing hydrogen species are bound to carbon, therefore, LPG dissociates less easily into the reactive reducing components on the pellet surface. When the pellet is exposed to reducing gas like LPG, it reacts with the chemisorbed oxygen and is adsorbed on the surface of the pellet then the exchange of electrons take place between the LPG and oxide surface upon adsorption i.e., a surface charge layer will be formed. When the LPG reacts with the surface oxygen ions of the composites, a potential barrier would be developed i.e., this mechanism involves the displacement of adsorbed oxygen species by formation of water. The overall reaction of LPG with the chemisorbed oxygen may take place as shown in figure 5.8[18].

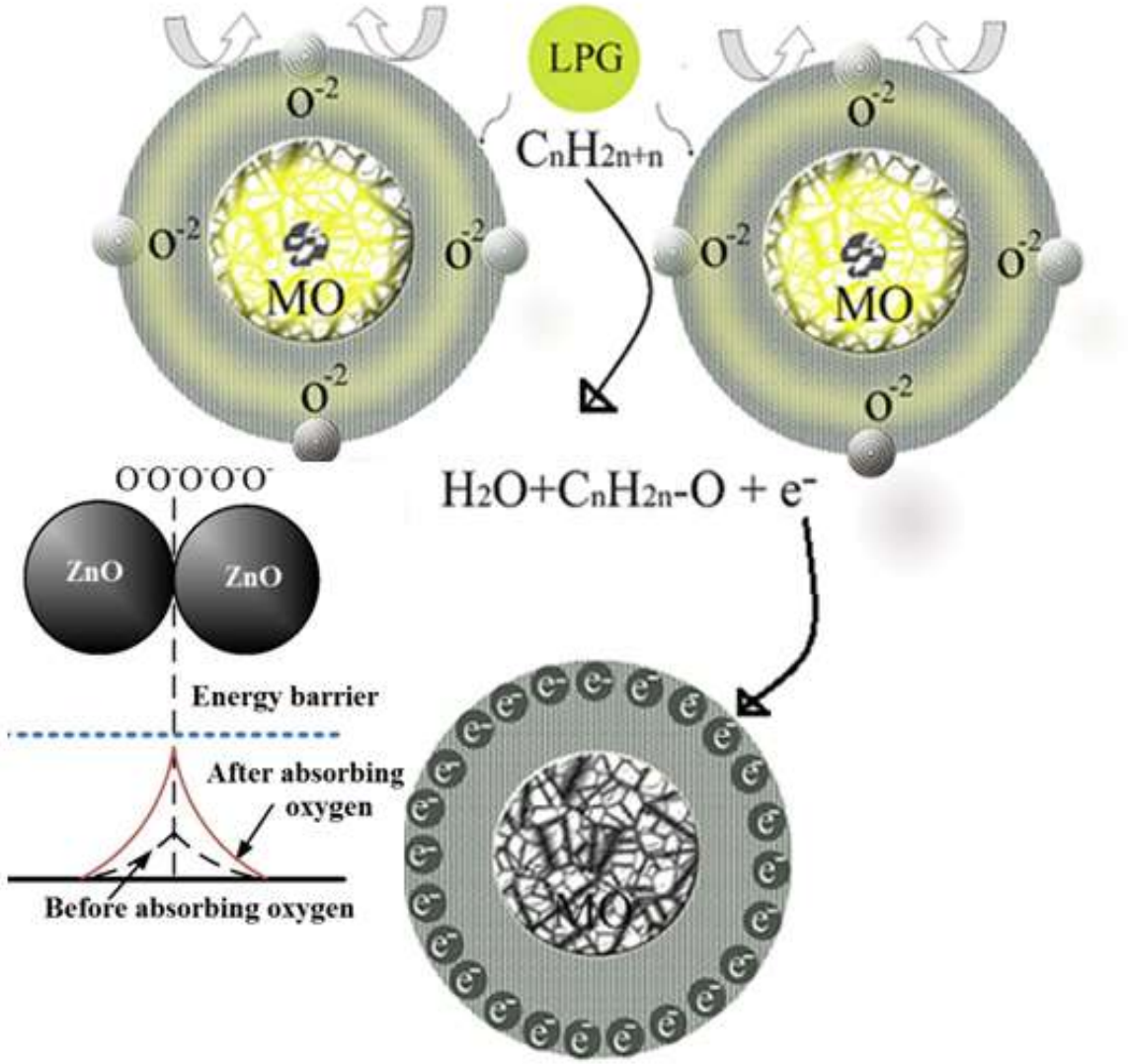

Figure 5.8 LPG sensning mechanisum of PANI – ZnO composites

5.9.6 Response to various test gases

Figure5.9 show the variation of selectivity of the PANI/ZnO nanocomposites for various gases such as Benzene, Toluene , Cyclohexane and LPG. It is expected here that different gases would produce different resistance response that are depending on catalytic activity of ZnOparticles. This could be used as a means to selectively distinguish between different gases. It can be seen that the response for Benzene and Toluene are negligibly small (≤ 20%) and for the Cyclohexane sensing response is less than 30% for different wt% whereas for LPG the maximum sensing response is found to be 87 % for 30 wt % of PANI – ZnO nanocomposites. The increasing in sensitivity and selectivity of PANI / ZnO nanocomposites is due to mesoporous structure.

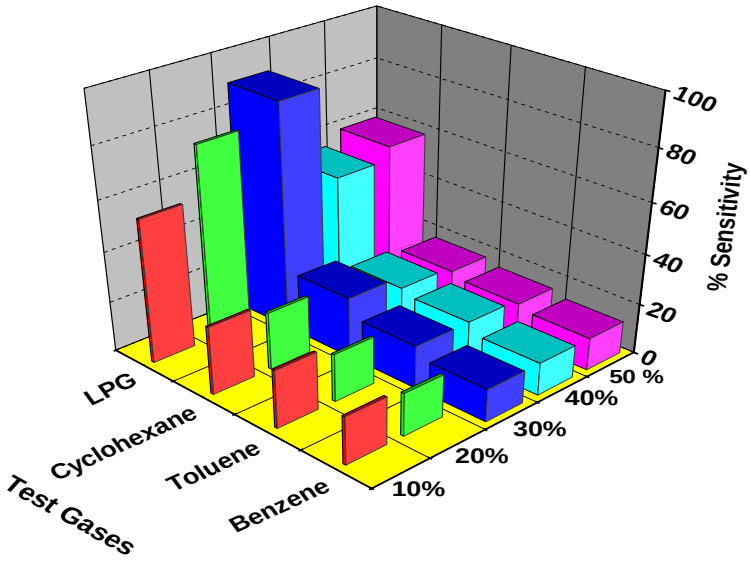

Figure 5.9 Shows response to various test gases

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