IJCTA, 9(41), 2016, pp. 273-278 ISSN: 0974-5572

Alkali Metal Salt-Polymer Composite doped with ZnO Nanoparticles: A Novel Material for Resistive Humidity Sensing

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ABSTRACT

A Humidity Sensor based on polymer electrolyte nanocomposite is fabricated in the present investigation.The nanocomposite is deposited on a ring shaped platinum and copper electrode for evaluating its sensing capabilities.The sensor shows change in resistance by 10times with variation of Humidity from 20-65 RH. Above 65 RH value of resistance becomes more or less constant.Working of the sensor us also assessed by variation with temperature and the sensor shoes best linear response at 35°C. To study the effect of ageing sample prepared was under investigation for 100 days . It was observed that nature of curve is same for complete 100 days but there is shift of about 3% in sensor response over a period of 45 days and it sustained even after 100 day. The composite film formed in the present composite sample has hysteresis value equal to 2.30%. The recorded response and recovery time of sensing composite is 53 sec and 321 sec.

Keywords: Humidity Sensor, Ageing, polymer

1. INTRODUCTION

Humidity sensors is being widely used in industrial processes and environmental management. Examining of humidity is one of the most important process in development of wafer for fabrication of ICs [1] in electronics industry, sterilization in medical field, green house conditioning in agriculture to defoggers in automobile industry. Mainly polymers play a very important role in sensing applications

Gas-detection sensors can be coated with a functional polymer layer. The absorption of an analyte, water vapor in particular, alters the physical properties of the polymer film which can be measured. There are several transduction techniques such as the gravimetric technique which detects the mass load of the polymer film by resonant cantilevers [2] or by quartz crystal microbalances [3]. The change of the dielectric constant can be measured by a capacitive technique [4] and the amount of heat that is generated in the polymer during absorption can be detected by a calorimetric transducer . Variation in resistance in a polymer electrolyte as observed on absorption of a analyst. [5-7]. Hygrometric method has been traditionally used to measure humidity which is based on change in volume of the polymer owing to absorption of water. This can be done by coating a silicon membrane [8] or thin single-clamped beam with an absorbent polymer layer .But the sensitivity of this sensor is very low.

The latest development in resistive type humidity sensor is to coat organic polymer so as to overcome the limitation of environment when condensation occurs. In these sensors, the organic polymer is used in the form of macromolecules in which a unit structure is repeated. Polyvinyl alcohol (PVA) is a cheap and common hydrophilic polymer. In presence of moisture it attracts – OH group at alternate carbon in its backbone [9-10] as shown below Fig. 1:

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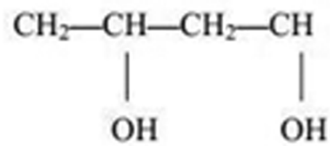

Figure 1: Chemical structure of PVA with water molecules.

Due to its high affinity to water, PVA film adsorbs moisture from the environment, thereby changing its resistance.PEG is formed by combination of Ethylene oxide and water.Most important attributed with PEG is its solubility in water and also many aromatic organic solvents.They are also widely used as plasticizers, emulsifying agent and water soluble lubricants.Room temperature conductivity of pure PVA is low but its intrication with PEG boosts up its conductivity. The present investigation intend to augment the conductivity of the polymer blend.

2. EXPERIMENTAL METHODOLOGY

2.1. Film Preparation

Commercial PVA polymer was procured from Sigma-Aldrich. Solutions were prepared by diluting PVA in distilled water followed by heating at 70 ÚC at 3 hours with constant stirring until viscosity is achieved by using magnetic stirrer. Potassium salt and zinc oxide nanoparticles were added to the solution and stirred at slow rate. Polyethylene glycol (PEG) was added drop by drop during stirring of 1 hour. The composite polymer solution was ready to make the film of electrodes for the sensor.

2.2. Preparation of Electrodes

Ring shaped electrodes having diameter approx 2cm of copper and platinum wire were prepared. These electrodes were submerged in the composite polymer solution and than removed slowly. An 18 micrometer film was deposited on these ring shaped electrodes which were further kept in oven at 58oC for 35 min. After this interval a uniform film was deposited on the electrode which will be used for sensing applications.

2.3. Measurements

For measurements ring shaped Copper electrodes was kept in chamber with controlled humidity and temperature. Two terminals of the electrode were connected to an electrometer as shown in Fig. 2. This operation was done for forward (increasing RH) as well as reverse(decreasing RH) reverse cycle.

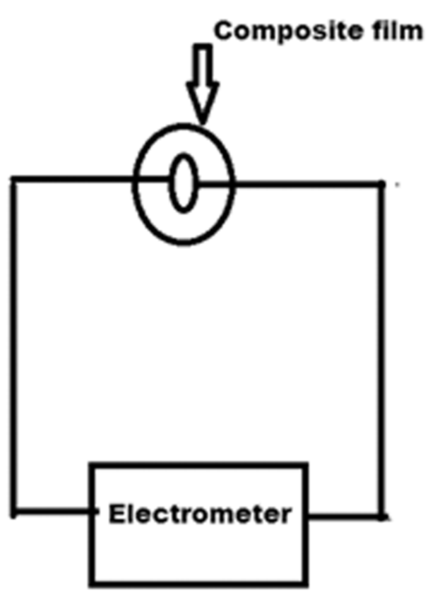

Figure 2: Measurement of Resistance vs RH

3. RESULTS AND DISCUSSION

In the present investigation ring electrodes of composite polymer films made of (i) PVA, PEG and alkalies (KOH, KCl) and (ii) films of PVA, PEG, alkalies with ZnO nanoparticles have been studied for humidity sensor. Results of resistance vs. RH of the composite film of PVA, PEG, ZnO and alkalis are shown in Fig. 3. It is observed that the resistance of the composite film has decreased by about 10 times, and linearity range expands from 30 RH to 65 RH. PVA based resistive humidity sensor has been reported by many authors [11-12]. Due to hydrophilic nature of the sensing material adsorbs water molecules in humid atmosphere. PEG is more hydrophilic than PVA, and by the presence of ZnO in the composite film its affinity for water is enhanced further. So, consequently, conductivity of the composite film is enhanced. The observation of the absolute linearity of resistance v/s RH for humidity range 30-60 RH, indicates the proportional decrease of resistance with increase of humidity, and thereby suggesting that the predominance increase of conductivity due to presence of ZnO [13]. At higher values of humidity, i.e beyond65% RH, the resistance becomes stable indicating the condensation of water molecules leading to saturation. There is enormous increase in conductivity at higher humidity. The composite film developed in the present investigation works for more than 100 days with the consistent efficiency indicating its mechanical stability, and thus, can be used for humidity sensor for a longer time. The most sensitive segment of the curve ranged from 40-60 RH and found suitable for humidity measurements.

The important characteristic feature associated with use of polymer as Humidity Sensor is that its physical properties should remain constant with respect to variation in operating conditions. The polymers used in the present investigation (PVA and PEG) shows stable conductivity values even at higher pH [14]. Hence, these polymers are best suited for electrochemical applications as in humidity sensing [15].

Apart from stable properties the material used should be sensitive, highle selective and must possess low detection limit[16]. Also it should be able to maintain its structure throughout the operating conditions and should offer minimum contact resistance[17].

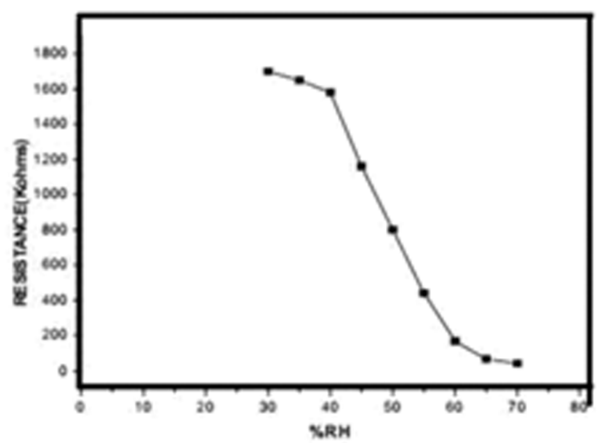

Figure 3: Resistance vs. RH for composite polymer (PVA + PEG + alkalies).

3.1. Effect of Temperature

Different samples of the ring type electrode were studied at various temperatures from 25 ºC to 40 ºC. It is observed that at 35ºC, the curve shows better linearity as compared to other temperature curves [Fig 4]. With further increase in temperature there is decrease in linearity of the curve before becoming constant. With increase in temperature, the resistance decreases, however nature of curve remained same. It is a well known fact that the physio-sorbed H^+ and OH^- present in the composite helps in humidity sensing [18-19]. As the temperature of the composite is increased kinetic energy of the adsorbed water molecules began to increase. So initially, there is enhanced movement of water molecules upto 45ºC (approx). This leads to decrease in resistance and increase in

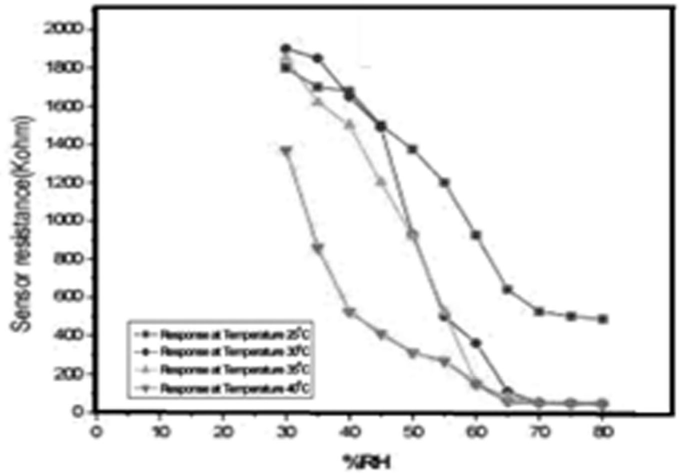

Figure 4: Resistance vs. RH at different temperatures.

conductivity of the sample upto 5ºC. On further increasing temperature water molecules gain more energy and has the tendency to leave the surface. So the values remain more or less constant [20].

3.2. Effect of Time

The composite sample prepared was under investigation for 100 days between different intervals of 1,15,30,45,100 days. It was observed that nature of curve is same for complete 100 days but there is shift of about 3% in sensor response over a period of 45 days and it sustained even after 100 day which is attributed to ageing(fig 5).Ageing occurs in sensors on account of extended introduction of the sensing element to water vapour and adsorption of water vapour at different sites on the material.More is the sensitivity of the material, the more it will be vulnerable to ageing[22-22]

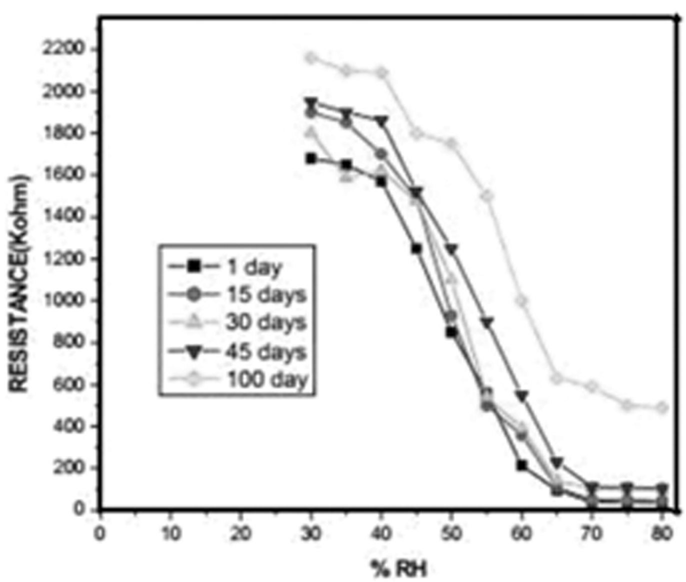

Figure 5: Resistance vs. RH for different durations.

3.3. Hysterisis

To study Hysteresis Effect, polymer was subjected to increasing humidity from 10-90% followed by reverse cycle of humidity from 90-10% (fig 6)

Humidity Sensors have Hy.Composite material prepared in the present investigation has hysteresis value of 2.45%.Commercially available steresis in the range 1.25-4.8% [23-24]

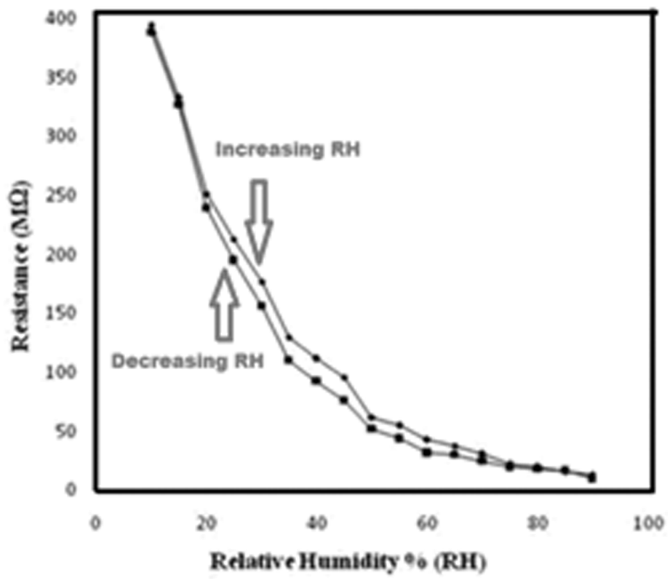

Figure 6: Hysteresis loop of the composite polymer

3.4. Recovery and Response Time

Response time for the sensor was estimated to be 52sec and the recovery time was 320 sec.Calculated time for recovery process is always more than that of response as time taken for desorption is more than the time taken for adsorption.[25]

4. CONCLUSION

The present investigation deals with fabrication of Humidity Sensor by doping PVA-PEG polymer blend with ZnO nanoparticle and it measures humidity in the range 30-60RH.

ACKNOWLEDGEMENT

Author acknowledges the management of Lovely Professional University for providing adequate facilities and Sharda University also for providing technical help.

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