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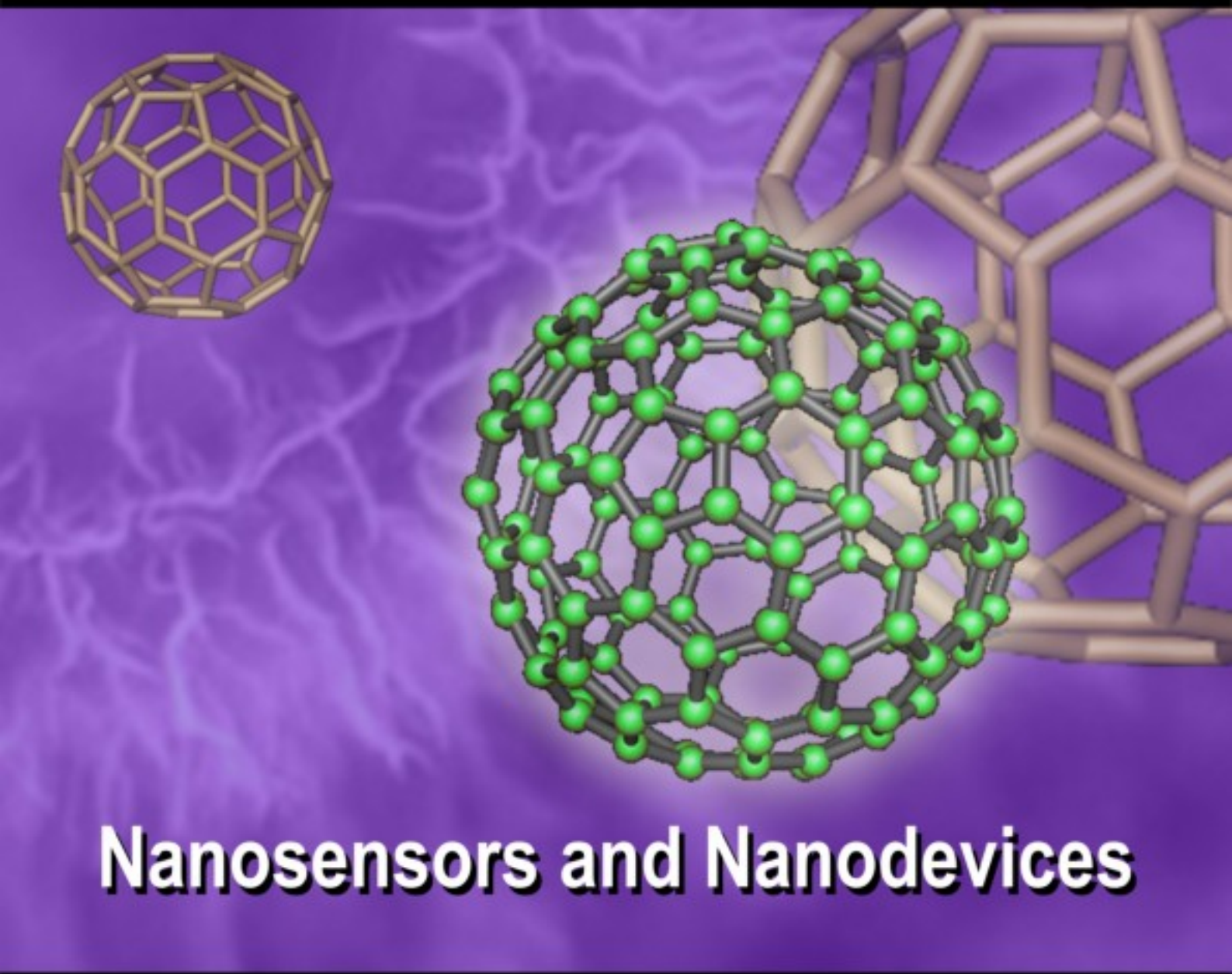

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Cross Linking Polymers (PVA & PEG) with TiO_2 Nanoparticles for Humidity Sensing

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Abstract: Humidity Sensors of different types are being used for various applications. Resistive Humidity Sensor has advantage over others for being small, low cost, interchangeable and long term stable. This makes them suitable for industrial, commercial and residential applications.

In the present investigation humidity sensing behavior of various composite films made of Polyvinyl Alcohol (PVA), Polyethylene glycol (PEG), alkalies and oxide nanoparticles has been studied. It was found that relationship of resistance v/s relative humidity (RH) was linear from 40 RH to 60 RH for a composite film made of PVA + PEG+ alkalies .The film can work with reliable efficiency for more than 100 days for the above range of humidity at room temperature.

In order to improve the efficiency of composite polymer film TiO_2 nanoparticles were added in the film and studied for resistance vs. RH responses. It was found that humidity range expands from 30 RH to 65 RH indicating the proportional decrease in resistance with increase in humidity at both ends as a result of the presence of TiO_2 nanoparticles. The composite film with TiO_2 nanoparticles can thus be used for wider range of humidity with reasonable stability and consistency.

The observed behavior of the film has been attributed to the transportation of charge through TiO_2 nanoparticles enhancing the conduction with the cross linked polymers. *Copyright © 2009 IFSA.*

Keywords: Relative Humidity, Poly ethylene glycol, Polyvinyl alcohol, Resistive humidity sensor, Titanium dioxide nanoparticles

1. Introduction

There is continuing need for accurate, reliable, inexpensive sensing systems for measuring relative humidity (RH). Sensors have wide applications in chemical industry, agriculture, process control and atmospheric sciences [1]. Automobile industry has large demand for rear-window defoggers and motor assemblies [2].

Polymer based sensors are attracting the attention of researchers owing to their interesting electrical properties and for their comparatively being cheaper. There have also been no reported studies on the humidity sensing characteristics of cross linking polymer materials. Polymers like polyvinyl alcohol (PVA) mixed with water show higher sensitivity at humidity (RH) sensing at room temperature. Humidity sensing membranes of polyelectrolyte containing amine was also reported [3]. The most important specifications while selecting a humidity sensor are accuracy, repeatability, long term stability, size, packaging and cost effectiveness.

There are two types of sensors - capacitive and resistive type. Resistive type is more useful because of their interchangeability. One measures the change, electric resistance or current of a film in a hygroscopic medium. The sensors consist of noble metal electrodes either deposited on a substrate or wires wound around a plastic or glass rod. 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 in the form of macromolecules in which a unit structure is repeated. PVA is a cheap and common hydrophilic polymer. In presence of moisture it attracts –OH group at alternate carbon in its backbone as shown below Fig. 1:

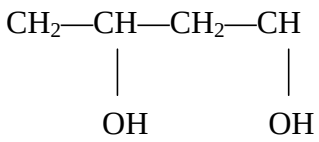

Fig. 1. Chemical structure of PVA with water molecules.

Due to its high affinity to water, PVA film adsorbs moisture from the environment, thereby changing its resistance. On prolonged exposure to moisture, it losses its durability. It absorbs and desorbs water from the moisture present in atmosphere. The electrical resistance of PVA film normally is very high but cross linking of PVA with some organic electrolytes, like sodium salts of 4-styrene sulphonate (SS), makes it water insoluble, and helps retaining its humidity sensing capabilities [4]. At low humidity (RH), the resistance is very high and the film is not sensitive enough to respond. Therefore suitable electrolytes are added to increase the sensitivity. The polymer chains are cross-linked and thereby improve the stability [5]. Generally, the polymers with polar groups like polyethylene oxide (PEO), Polyvinyl pyrrolidone (PVP) have been used as dopant material with different ammonium salts and acids [6,7].In the present investigation the resistive type humidity sensor has been developed from the composite polymer film of PVA and PEG as a host polymer matrix, and NaOH and NaCl as dopant salts. At room temperature conductivity of pure PVA is very low, but complexing it with PEG and dopants enhances its conductivity. This paper reports the results of resistive type humidity sensor made of composite polymer film with TiO_2 nanoparticles. The mechanism of charge conduction increasing the durability of the film electrode and its response to temperature and time has been discussed.

2. Experimental

2.1. Film Preparation

1. Commercial PVA polymer was obtained from M/S Scharlau Chemie, Sentmenat Barcelona (Spain) and used in the present work. Solutions were prepared by diluting 10 gm of PVA in water. The solutions were heated at 70 ˚C for 3 hours in a beaker and shaken by a magnetic stirrer. When they became dense, the heating process was stopped and left to cool down. Salts of NaCl (0.1 gm) and NaOH (0.05 gm) and TiO_2 nanoparicles were added to the solutions and stirred at slow rate. Poly ethylene glycol (PEG) was added drop by drop during stirring of 1 hour. The composite polymer solution was ready to make the film electrodes for the sensor.

2.2. Preparation of Ring Type Electrodes

For using the film, ring electrodes of copper wire varying in diameter from 1.5cm to 1.8 cm were prepared. The ring electrodes were dipped one by one in the composite polymer solution and slowly taken out. The electrodes were kept in an oven at 60 ˚C for 30 minutes. Dipping time and drying time controls the film thickness. Film of about 20-micrometer thickness was thus prepared for ring type electrodes of different diameter.

2.3. Measurements

For recording the measurements, the ring electrode was kept in a humidity-controlled chamber where humidity of the film could be maintained at particular temperature. Two terminals of the electrode were connected to an electrometer as shown in Fig. 2. Humidity was gradually raised and controlled at a particular temperature and the corresponding resistance was recorded. This was done for ascending and descending cycles of humidity for each sample.

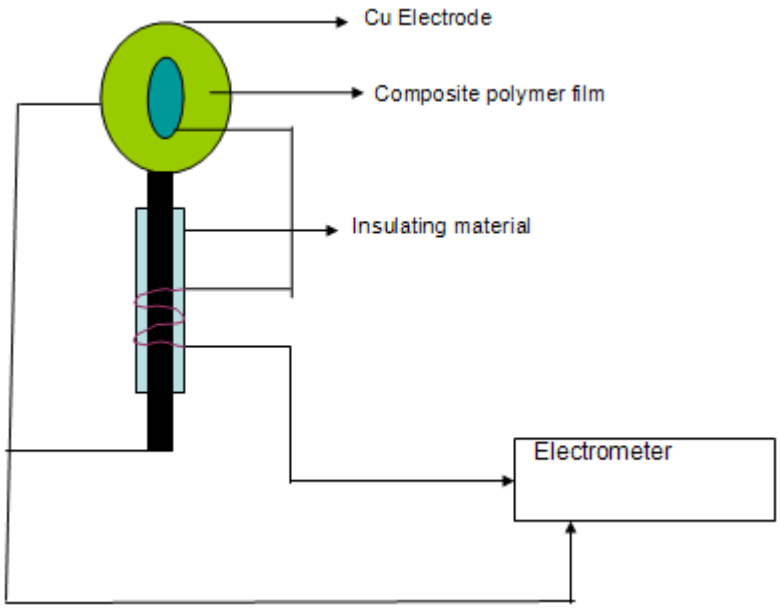

Fig. 2. Working principle of ring type electrode.

3. Observations and Results

Fig. 3 shows Resistance vs. RH of the ring electrode prepared from the solution of the composite polymer (PVA+PEG+NaOH+NaCl) at room temperature (35 ˚C). The curve is linear for 40-60 RH range. On the lower side there was a sudden drift at 40 RH and thereafter the curve shows linearity between 30-40 RH. This shows that the resistive type sensor could conveniently be utilized for the above two linear ranges. It was seen that at lower values of humidity, i.e., 30-40 RH, the sensitivity decreases as compared to 40-60 RH range. Sensitivity also goes down at higher values of humidity i.e., >75 RH. 40-60 RH range of the curve is the most sensitive and thus is suitable for humidity measurements.

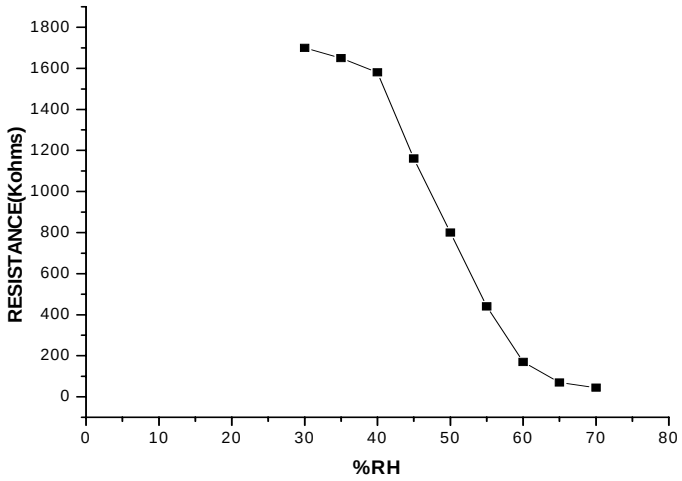

Fig. 3. Resistance vs. RH for composite polymer (PVA +PEG+ alkalies).

3.1. Effect of Temperature

Samples of the ring type electrodes were studied under different temperatures ranging from 25˚C to 35 ˚C. Fig. 4 shows the results of Resistance vs RH at 25 ˚C, 30 ˚C, 35 ˚C and 40 ˚C. It was observed that the curve shows better linearity at 35 ˚C (room temperature) as compared to the curves at 25 ˚C or at 40 ˚C. With the increase in temperature, the resistance decreases, however the nature of the curves remains the same.

3.2. Effect of Time

A single sample was studied at intervals of 1, 15, 30, 45 & above 100 days. Fig. 5 shows the results of Resistance vs. RH. It was observed that nature of curve is same with sensor response shift within $\pm$3 %, over a period of 45 days and it sustained even after 100 days. Thus the results indicate that the aging of the film is moderately low. The film has shown sustained stability for RH sensing even after 100 days.

Results of resistance vs. RH of the composite film of PVA +PEG+TiO_2 and alkalis are shown in Fig. 6. It is noted that the resistance of the composite film has increased by about 10 times, and linearity range expands from 30 RH to 65 RH.

Measurements of Resistance vs. RH were taken for ascending and descending orders for the same sample and the comparison graph is shown in Fig. 7. It was noted that both the curves are almost identical indicating the reproducibility of the results.

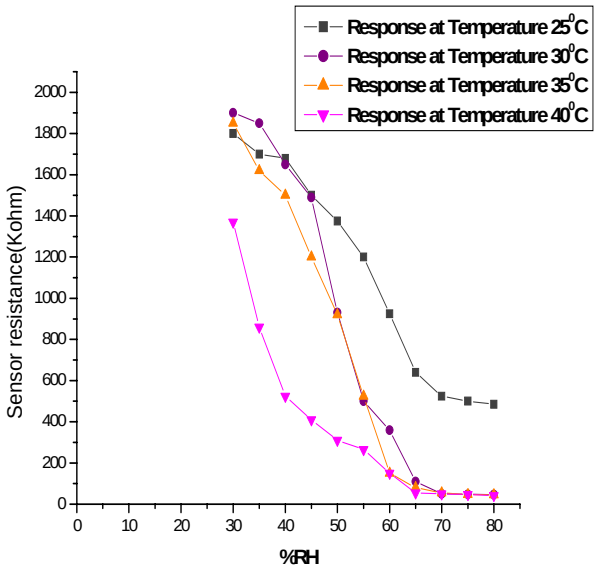

Fig. 4. Resistance vs. RH at different temperatures.

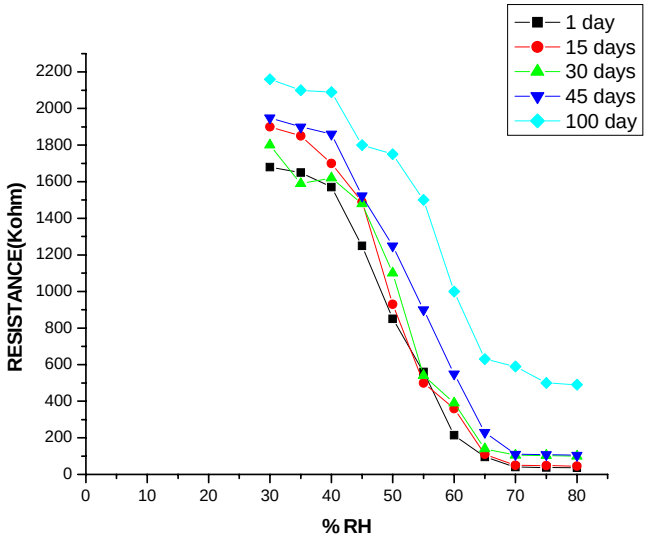

Fig. 5. Resistance vs RH for different durations.

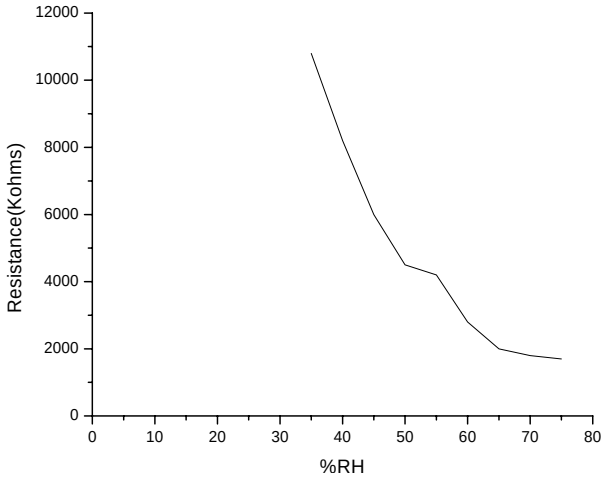

Fig. 6. Resistance vs. RH for composite polymer (PVA +PEG+TiO_2 + alkalies).

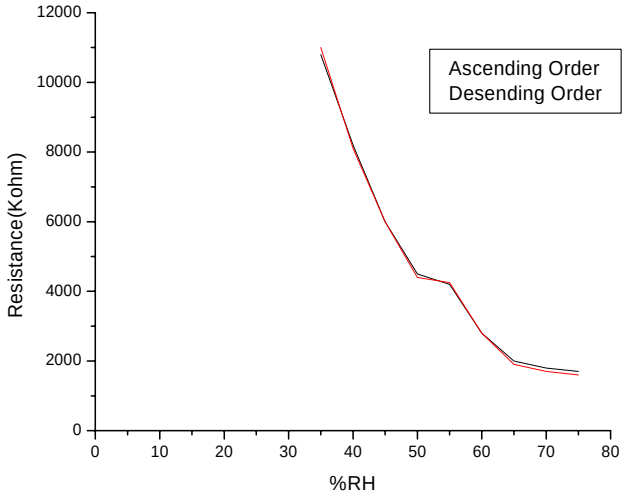

Fig. 7. Resistance vs. RH for composite polymer (PVA +PEG+TiO_2+alkalies) for ascending and descending order.

4. Discussion

In the present investigation ring electrodes of composite polymer films made of (i) PVA, PEG and alkalies, and (ii) films of PVA, PEG, alkalies with TiO_2 nanoparticles have been studied for humidity sensor. PVA based resistive humidity sensor has been reported by many authors [8, 9]. PVA is a non conducting polymer, but because of this being hydrophilic, it adsorbs water molecules in humid atmosphere. PEG is more hydrophilic than PVA, and its presence in composite film enhances the affinity to absorb more water molecules. Consequently, it increases the conductivity of composite polymer film.

Linearity of the curve for the humidity range 40RH to 60 RH indicates the suitability of the composite film for better sensing material. The observation of the expansion of linearity for resistance v/s RH from 30 RH to 65 RH, indicates the proportional increase of conductivity even at lower and higher values of RH due to the predominance of TiO_2 nanoparticles. At higher values of humidity, i.e., beyond 65 RH, the resistance becomes stable with increase of humidity. This may be due to condensation of larger number of water molecules, which leads to their saturation. There is enormous increase in conductivity at higher values of humidity. This is the same situation as explained by Grotthuss mechanism of protonic conduction, which may be holding in the composite polymer electrolyte at higher humidity.

That, the composite polymer film, developed in the present investigation works for more than 100 days with consistent efficiency suggests its mechanical stability at longer range of humidity. It is, therefore concluded that the composite polymer film made of PVA, PEG, alkalies and TiO2 nanoparticles works well for humidity sensor and a resistive type humidity senor could be fabricated for humidity range 30 RH to 65 RH.

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Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc.

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Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

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- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
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- Nanosensors;
- Microsystems;
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