Organic Cu/cellulose/ PEPC/Cu humidity sensor

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In this study an investigation has been made on the electrical properties of Organic Humidity Sensors being fabricated by the use of cellulose and poly-N-epoxypropylcarbazole (PEPC). The 2 wt% of cellulose and 4 wt% of PEPC were blended in Benzol. In the fabrication of Cu/Cellulose/PEPC/Cu sensor, a composite thin film was deposited on copper electrodes by drop casting. The electrodes were deposited by sputtering process in which the gap between the electrodes was kept as 45 µm. The capacitance and dissipation of the sensors were measured under the effect of relative humidity. It was found that the capacitance and dissipation of the sensor increased 21 and 81 times respectively with increase of the Relative Humidity (RH) ranging from 45%-89%. By measured capacitance and dissipation, the resistance and impedance were calculated. The capacitance and resistance-humidity relationships showed significant change in the range of 67%-89% RH and 45%-83% RH respectively. The impedance-humidity relationship demonstrated more uniform changes in the range of 45%-89% RH relative to the capacitance and resistance-humidity relationships. Humidity dependent properties of the sensor make it attractive to be used in capacitive, resistive and impedance type humidity sensors, thus it can be used in the humidity meters for environmental monitoring and assessment purposes.

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1. Introduction

Sensing devices play an important role in our modern age. Sensors are used for meteorology, security, intelligence, industrial production and safety, building air-conditioning, environmental monitoring, health caring, agricultural development, pharmaceutical, medical and food industry [1-8] etc. The measurement of humidity is frequent because of the universal existence of water, which affects physical properties of materials [9] and health of human beings.

Humidity sensors are also used in all above mentioned applications [1, 10]. Depending upon the basic sensing principles, humidity sensors are classified as resistive, capacitive, thermoelemental [11] oscillating and mechanical [10]. Each type of sensors has specific application based on its unique advantages. Required parameters for efficient and commercially acceptable humidity sensor are wide range sensitivity, high accuracy, linear response, [3] short response and recovery time, small hysteresis, [11] long term physical and chemical stability, low power consumption and low cost [12]. For fabrication of humidity sensors, organic and inorganic materials are used [13] in the form of ceramics, composites and conducting polymers [12]. Among these materials, conducting polymers are the most suitable [14] because of their low cost, ease of fabrication, flexibility, quick response, high sensitivity, [15, 16] environmental friendly and simple technology [17].

The capacitive type humidity sensors are fabricated by hydrophobic polymers while the resistive sensors are fabricated by polymer electrolytes [12]. Sensors are investigated in two designs; one is Surface Type Configuration and other, which is mostly used, sandwich configuration. It has been found that Sandwich type devices carry some demerits like complex technology, expensive processes and short circuiting, while surface type devices provide the best alternative due to their simplicity and lower cost [18]. Organic semiconducting materials have great potential due to their electric, optical and dielectric properties, but they need modification [2].

For humidity sensing polymers are used in their original form, polymers blend, doped polymers, copolymers or polymer composites with organic and inorganic semiconducting materials [19-22]. The working principles of humidity sensing polymers are different. Ionic polymers are based on variation of electrical conductivity or resistance with adsorption of water molecule [21]. The adsorption or desorption of water molecule causes a change in the dielectric constant of the polymer thin film lying between two electrodes. This change in dielectric constant in capacitive type humidity sensors can be explained by this equation [15].

$$C = \frac{\varepsilon A}{d} \tag{1}$$

where C is the capacitance, ε is permittivity, A is area of electrode and d is the gap between two electrodes. In resistive type humidity sensors upon adsorption of water molecules produce conductive ions due to ionization of polymer electrolyte [12] or changes due to doping. Generally with the increase in humidity and by dissociation of mobile carriers the conductivity of a polymer electrolyte increases [23].

Concurrently high sensitivity and resistivity to water molecule are the required properties for humidity sensing materials [12]. Some organic polymers are highly sensitive at low humidity but due to their dissolution in water they can not be used at higher humidity [2, 24]. For humidity sensors, suitable materials are water insoluble organic compounds like polyimide and cellulose acetate butyrate [24] and cross linked poly (methyl methacrylate) [25]. Cellulose and PEPC are water insoluble materials [26], previously Metal/cellulose/Metal hygrometers [27] and Poly-N-epoxypropylcarbazole complexes photocapacitive detectors [28] were fabricated in our institute.

The formation of charge transfer complexes of PEPC with low molecular organic materials make it electrically conductive and highly photosensitive [29]. PEPC and its derivatives due to their photosensitivity and adhesiveness [28] have potential for fabrication of majority of organic semiconductor devices like sensors, solar cells, recording media in electrography and photoelectric convertors [30]. In the present work it has been endeavored to develop a humidity sensor which may show good sensitivity over a long range relative humidity level. Therefore a humidity sensor, based on the blend of thin film of poly-N-epoxypropylcarbazole (PEPC) and cellulose composite, has been fabricated.

2. Experimental

For the fabrication of humidity sensor, PEPC was synthesized in laboratory [28] and a commercially available cellulose ($(C_6 H_{10}O_5)_n$) having density of 1.592 g/cm^3, was used. The cellulose was used in as received form. Fig.1 and Fig.2 show the molecular structures of PEPC and cellulose. The suspension of 2 wt% cellulose was prepared in a solution of 4 wt% PEPC in benzol. Glass substrates were cleaned in BANDELIN SONOREX RH100H sonicator for 13 minutes using by methanol. After drying the glass substrates, the metallic electrodes were deposited by using ADWARD S150B sputter coater. The thickness of the electrodes was 100 nm and between two electrodes there was a gap of 40 µm, while the gap length was 15 mm. Approximately 100 µm thick film of PEPC and cellulose composite, was deposited by drop casting method. The fabricated devices were dried at room temperature for 20 hours. The schematic diagram of the Cu/Cellulose/PEPC/Cu humidity sensor is shown in Fig.3. Capacitance and dissipation with respect to relative humidity were measured by using indigenously made humidity chamber (which was fabricated in our laboratory), and digital display LCR meter ESCORT ELC–3133A. Humidity and temperature inside the humidity chamber are measured by the digital hygrometer, made by Fisher Scientific. The results of measurements were recorded and used for the calculation of resistance and impedance.

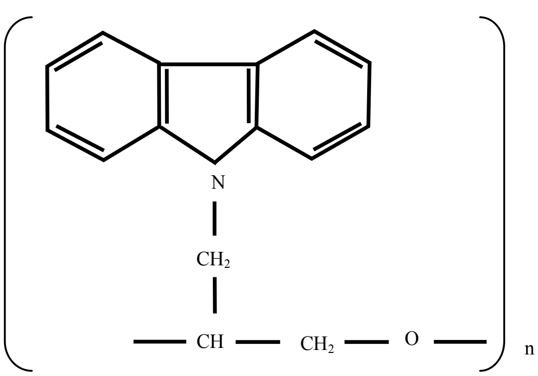

Fig. 1. Molecular structure of poly-N-epoxypropylcarbazole.

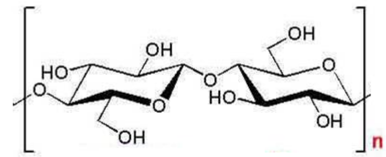

Fig. 2. Molecular structure of cellulose.

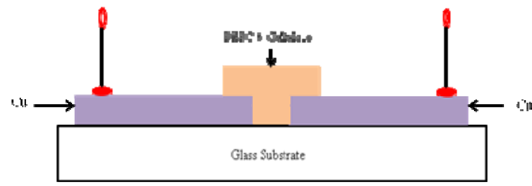

Fig. 3. Cross-sectional view of the Cu/ Cellulose /PEPC /Cu sensor.

3. Results and discussion

The relationship among capacitance, resistance, impedance and relative humidity for the Cu/ Cellulose/PEPC/Cu humidity sensor at a frequency of 1 KHz is shown in Fig.4. Graph of Capacitance versus Relative Humidity shows that the capacitance initially increased in a gradual mode from 67 % - 80 % RH but abruptly a huge change occurred in the humidity range of 80 % - 89 % and capacitance increased 21 times. Capacitance response covers a short range of humidity. It is also evident from the Fig.4 that upto 89 % relative humidity, the resistance decreases by 1740 times with respect to 45 % RH. The reasons behind this increase of capacitance and decrease of resistance with increase in humidity may be the following [27-31]:

i. Absorption of water molecule in semiconductor thin film which increases the dielectric constant and decreases the resistance due to displacement current.

ii. Doping of the organic material by H_2O molecule.

iii. Formation of charge transfer complexes.

The resistance (R) of the sample was determined from the values of dissipation (D) from the following expression [32].

$$R = \frac{1}{6.28\, f\, C\, D} \tag{2}$$

where *f* is frequency and *C* is capacitance

Although the resistance response covers a wide range of humidity as compared to capacitance response but the response range is still short. Impedance-Humidity relationship in Fig.4 shows that impedance reveals a response of wide range of humidity from 45 % to 89 % RH. This is the total impedance of capacitance and resistance connected in parallel. Impedance was calculated by the following equation [32].

$$Z = \frac{1}{\frac{1}{R} + j\, 6.28\, f\, C} \tag{3}$$

where is R is resistance, *f* is the frequency and *C* is the capacitance.

The Impedance Humidity relationship of the sensor shows that with increase of humidity the impedance of sensor decreases. The more uniformity of impedance curve as compared to capacitance and resistance curve is due to the alterations in capacitance and resistance. With the increase in humidity, the simultaneous decrease in impedance and resistance reflects that resistance strongly affects the impedance as compared to capacitance.

There are a number of factors which affect the capacitance of the sensor. They are relative dielectric constant of the thin film material, area of electrodes, and gap between electrodes. Capacitance relies upon material's polarizability, sources of which are electronic (α_e), dipolar (α_{dip}) and ionic (α_i) [33]. Another form of polarizability due to transfer of charge carriers (electrons and holes) at normal conditions is also reported [31, 34-35]. In general due to relative displacement of orbital electrons, electronic polarizability occurs, which possibly at higher frequencies (>1000 Hz) affect the capacitance measurements. It is assumed on the basis of sensor response, that the absorption of water molecules in cellulose-PEPC composite thin film increases dipolar polarizability of sensor.

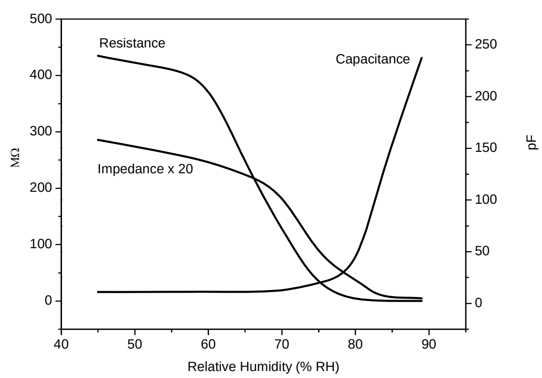

Fig. 4. Relationship among capacitance, resistance, impedance and relative humidity.

The simulation of capacitance to relative humidity relationship is done by Clausius-Mosotti relation [33].

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N_n \alpha_n}{3\varepsilon_0} \tag{4}$$

where ε is relative permittivity, N_n is concentration of water molecules at normal conditions, and ε_o is permittivity of free space. From above Eq.5 has been derived by considering the proportionality of capacitance with permittivity [8, 27].

$$\frac{C_H}{C_n} = \frac{[1 + 2N_n\alpha_n(1 + k_1\Delta H)/\,3\varepsilon_0]}{[1 - N_n\alpha_n(1 + k_1\Delta H)/3\varepsilon_0]\varepsilon} \tag{5}$$

where C_H is capacitance under effect of humidity, C_n capacitance at normal conditions, ΔH is change in relative humidity (ΔH = H-H_o, initial relative humidity H_o = 45 %), k_1 is humidity capacitive factor. For PEPC matrix the relative permittivity is assumed to be equal to 4 [28]. The value of k_1 determined by above expression for this case is 0.02117.

Fig. 5 shows the comparison of experimental and simulated capacitance with respect to relative humidity. It can be seen that there is a reasonable matching in the experimental and simulated curves.

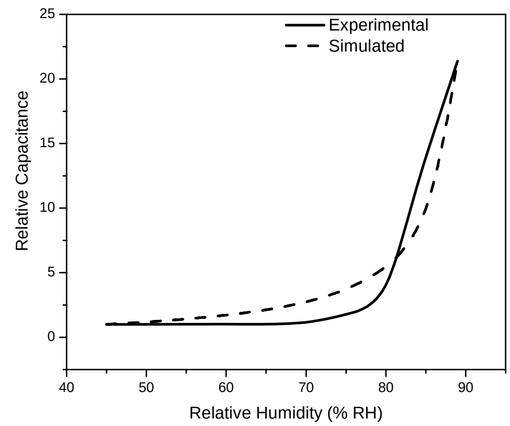

Fig. 5. Comparison of experimental and simulated capacitance with respect to relative humidity.

Simulation of the resistance-humidity relationship is done by following equation [36]

$$R = \frac{L}{\sigma A} = \frac{L}{qp\mu A} \tag{6}$$

where A is the area, L is the gap between two electrodes, σ is the conductivity, q is charge, p is concentration of charges and μ is mobility of charge carriers.

The above equation is based upon following assumptions:

i. Water molecules act as dopant.

ii. Electronic conductivity and displacement current are take place.

At initial humidity the relative resistance with respect to R_o (initial resistance) can be expressed as:

$$\frac{R}{R_0} = \frac{\rho_0\mu_0}{\rho\mu} \tag{7}$$

where p_o and p are the concentrations and μ_o and μ are the mobilities of charges at initial and higher humidity levels respectively. As the equation for determination of concentration of dopands [36] for example water molecules at the surface (C_s) and in the bulk (C) of the composite is:

$$C(x, t) = Cs\ erfc\ \{ x / 2 \sqrt{Dt} \} \tag{8}$$

In above equation x is distance from the surface, t is time and D is the diffusion coefficient. If in the absorption process D is approximately taken constant, then $C(x, t)$ is linear proportional to C_s. Hence it may be considered that

$$\rho\mu = \rho_0\mu_0 \frac{A + B\,\Delta H + (\Delta H/35)^7}{A} \tag{9}$$

where A and B are constants with values 3.3×10^{-2} and 1.1×10^{-4} respectively. By putting the value of pμ in Eq. 7, we get,

$$\frac{R}{R_0} = \frac{\rho_0\mu_0}{\rho_0\mu_0}\left(\frac{A}{A + B\Delta H + (\Delta H/35)^7}\right) \tag{10}$$

Hence

$$\frac{R}{R_0} = \frac{A}{A + B\Delta H + (\Delta H/35)^7} \tag{11}$$

Comparison of experimental resistance-humidity relation ship and its simulation is shown in Fig. 6. It is evident from the figure that the simulated values of resistance fall closest to the experimental values.

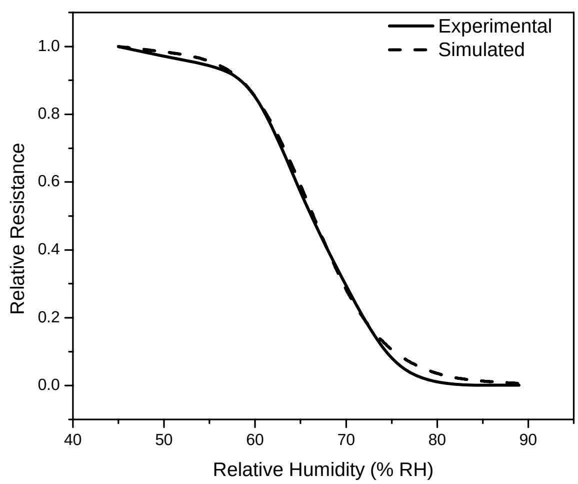

Fig. 6. Comparison of experimental and simulated resistance with respect to relative humidity.

Simulation of impedance can be derived by using the following equation.

$$\frac{Z}{Z_0} = \frac{A}{A + B\Delta H + (\Delta H/30)^{12}} \tag{12}$$

Simulated impedance-humidity relationship in comparison with experimental results is also shown in Fig. 7.

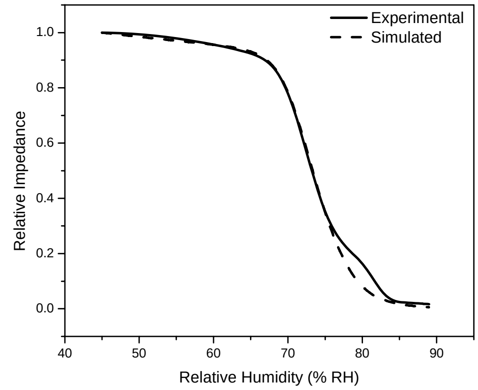

Fig. 7. Comparison of experimental and simulated impedance with respect to relative humidity.

The simulated results of capacitance are reasonably close to experimental results as indicated in Fig. 5. Although the simulated resistance and impedance are exactly same as the experimental results but there is slight deviation from experimental results in the humidity range of 75% to 83 %, which needs further improvement. In this regard the future work will be devoted to optimization of simulation approximation in order to make simulation results more close to experimental data.

4. Conclusions

A surface type humidity sensor based on cellulose and PEPC composite thin film was fabricated and investigated. The effect of relative humidity on capacitance, resistance and impedance of sensor was studied in the humidity range of 45 % to 89 %. Results revealed that with increase in humidity, capacitance increases and resistance and impedance decreases. Although capacitance and resistance-humidity relationships showed significant changes in the range of 67%-89% RH and 45%-83% RH respectively but impedance-humidity relationship demonstrated more uniform change in the range of 45%-89% RH. Due its wide sensing range and uniformity in behavior impedance humidity relationship is suitable for designing a cheaper, simpler and efficient meter for the measurement of humidity for the purpose of environmental monitoring.

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