Impedance hygrometer based on cellulose and CuPc

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Abstract: An investigation has been made on the properties of an impedance hygrometer fabricated using cellulose and copper phthalocyanine (Ag/cellulose/CuPc/Ag). A 5wt% suspension of cellulose was prepared in water while the CuPc was dissolved in methanol. Cellulose film was deposited on glass substrates with preliminary deposited metallic electrodes followed by deposition of CuPc film. The resistances and capacitances of the samples were evaluated under the effect of humidity. The impedance was calculated from resistance and capacitance measurements. It was also measured during the experiment. It was observed that the capacitance of the sensor increases and resistance and impedance decrease with an increase in the relative humidity level. It was found that the impedance–humidity relationship showed more uniform changes in the interval of 31%–98% RH than the resistance– and capacitance–humidity relationships that showed visible changes in the humidity intervals of 31%–80% RH and 80%–98% RH respectively. The humidity-dependent impedance of the sample makes it attractive for use in impedance hygrometers. The impedance hygrometer may be used in instruments for the environmental monitoring of humidity.

Key words: cellulose; copper phthalocyanine; organic; hygrometer; humidity; impedance
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1. Introduction

Many potential applications of organic semiconductors may be realized by investigation and modification of their electric, dielectric and optical properties[1−5]. At present, some organic semiconductors are used in commercially produced light emitting diodes. Some other organic semiconductors are very sensitive to humidity[1,2], temperature[5,6], IR, visible and UV radiation[7], and different types of gases[8]. Therefore, investigation of the physical properties of organic semiconductors under different conditions is very promising for the development of various sensors for humidity, temperature, light, radiation, strain, gases, etc. Undoubtedly, organic semiconductors will find more niches among electronic materials in the near future. There are various types of humidity sensors. Each type offers its distinct advantages. At present in resistive hygrometers, the most common material that is used is lithium chloride[9,10]. A mixture of lithium chloride and carbon is put on an insulating substrate between metal electrodes and forms a bulk type sensor. The resistance of the element decreases with increasing humidity, and this may be due to the formation of some energetic disorders in the element. The resistance of the hygrometer should be measured by applying AC to a Wheatstone bridge or by a combination of current and voltage measurements[9,10]. DC voltage is not applied because it tends to break down the lithium chloride to lithium and chlorine atoms. The resistive hygrometer must either be operated in a constant temperature environment or temperature corrections must be incorporated. Response times are typically of the order of a few seconds[9,10]. The resistance of the hygrometer varies from 10 kΩ to 10^3 MΩ as the humidity changes from 100% to 0%. Ceramic materials such as Al_2O_3 are also used in many commercial humidity sensors[11] due to the well established etching technology and temperature stability, but are very sensitive to dust and smoke, and their response time is very long.

Some organic compounds also show a high response to humidity but these compounds dissolve in water[12,13]. Such compounds are not suitable for hygrometers. Organic materials that are insoluble in water such as cellulose acetate butyrate and polyimide have been used as humidity sensors[13]. Orange dye (OD), a p-type organic semiconductor, has potential applications for humidity sensors[14,15]. As an OD exhibits high sensitivity towards humidity[16,11] it can be used as a resistive hygrometer.

Last year a number of capacitive and resistive humidity sensors were fabricated and investigated by our group on the basis of porphyrin and copper phthalocyanine[12,17−19]. These sensors showed good capacitive sensitivity at higher humidity and high resistive sensitivity at lower humidity. Investigation of the capacitive type humidity sensors fabricated by using cellulose and copper phtalocyanine (CuPc) showed that the sensor is more sensitive when the humidity is above 50%[19]. The sensor fabricated on the basis of cellulose was less sensitive than the sensor made on a double layer of cellulose and CuPc[19]. In this device the thicknesses of cellulose and CuPc films were 50 μm and 10 μm, respectively.

As a continuation of our efforts in fabrication and investigation of humidity sensors based on cellulose and CuPc[19], we report here the fabrication and investigation of an impedance hygrometer based on cellulose and CuPc.

2. Experimental

Commercially available cellulose with molecular formula $(C_6H_{10}O_5)_n$ and CuPc purchased from Sigma Aldrich were used without further purification for the fabrication of the bi-layer impedance hygrometer. The density of the cellulose

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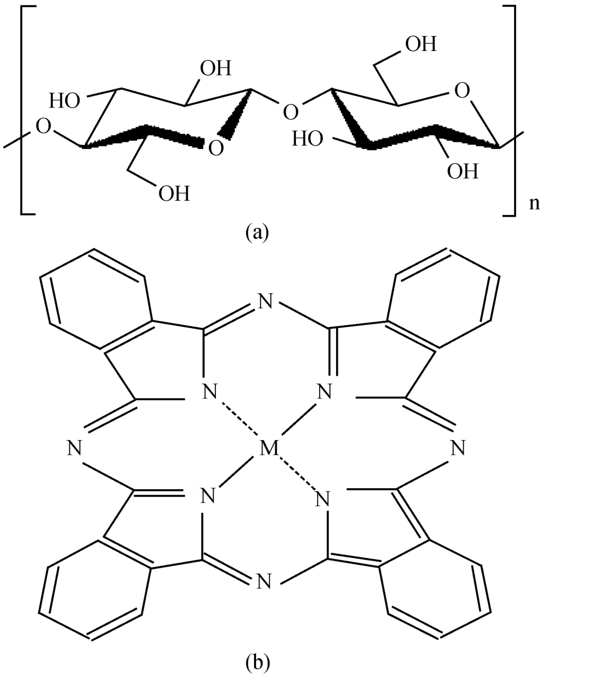

Fig. 1. Molecular structure of (a) cellulose and (b) copper phthalocyanine (CuPc).

was 1.592 g/cm^3. The molecular structures of the cellulose and CuPc are shown in Fig. 1. A 5wt% suspension of cellulose was prepared in water while the CuPc was dissolved in methanol. Glass substrates were cleaned for 10 min using distilled water in an ultrasonic cleaner and dried. Then the substrates were also plasma cleaned for 5 min. Metallic electrodes were deposited on the cleaned substrate, keeping a 50 μm gap between them. The thickness of the electrodes was 100 nm whereas the gap lengths were 5 mm. Films of cellulose and CuPc were deposited in sequence by the drop casting method with approximate thicknesses of 140 μm and 10 μm, respectively. To optimize the hygrometer's impedance, first of all the layer of cellulose was deposited and its thickness was measured; after that the layer of CuPc was deposited, the total thickness of the two layers was measured and the thickness of CuPc was estimated by subtracting the cellulose film thickness from the total thickness. Samples with cellulose thickness 215 μm and CuPc thicknesses 6 μm and 24 μm were also fabricated. Experimentally it was found that, from the point of view of uniformity of the impedance–humidity relationship, the optimal thicknesses of the cellulose and CuPc were 140 μm and 10 μm respectively. The fabricated devices were kept at room temperature for one night to evaporate moisture from the films. Figure 2 shows schematic diagrams of the fabricated Ag/cellulose/CuPc/Ag hygrometer. Measurements were carried out in self made humidity measurement setups, which have been developed in our device testing laboratory. For the measurements a hermetically sealed (by glass and polymer) cylindrical chamber was used. The volume of the chamber was 500 cm^3. For the measurement of *in situ* humidity and temperature a digital integrated hygrometer-thermometer-dew point from Fisher Scientific, USA and a water pulverizer were used. The humidity in the chamber was changed by pulverization of the water.

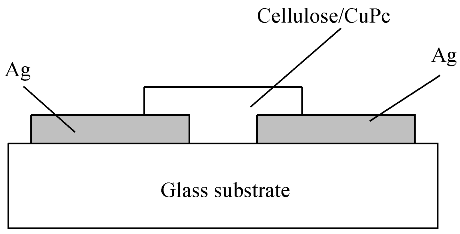

Fig. 2. Cross-sectional view of the fabricated Ag/cellulose/CuPc/Ag hygrometer.

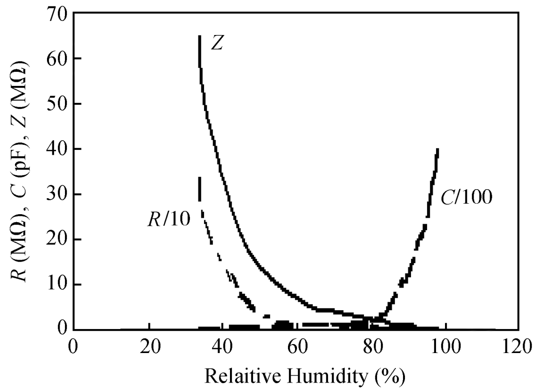

Fig. 3. Capacitance (C), resistance (R) and impedance (Z) versus relative humidity (H) relationships for the Ag/cellulose/CuPc/Ag hygrometer at a frequency (f) of 120 Hz.

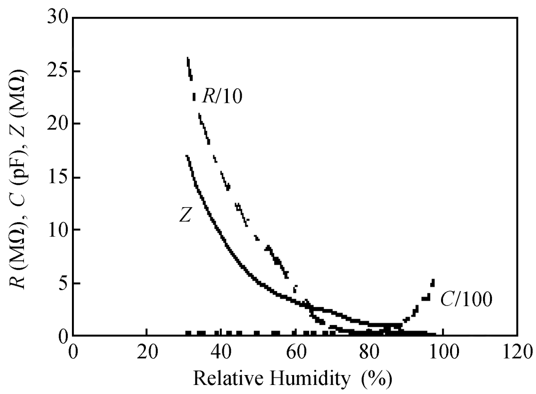

Fig. 4. Capacitance (C), resistance (R) and impedance (Z) versus relative humidity (H) relationships for the Ag/cellulose/CuPc/Ag hygrometer at a frequency (f) of 1 kHz.

3. Results and discussion

Figures 3 and 4 show capacitance (C), resistance (R)– and impedance (Z)–relative humidity (H) relationships for the Ag/cellulose/CuPc/Ag hygrometer at two different frequencies (f) of 120 Hz and 1 kHz. It is seen that the resistance shows a very sharp decrease in the interval of humidity of 31%–80%, and the capacitance shows a large increase in the interval of humidity of 80%–98%. The change in the resistance and capacitance of the hygrometer over the entire humidity interval was equal to 3300 and 210 at 120 Hz, and 2600 and 52 at 1 kHz. It is obvious that the hygrometer shows better performance at a frequency of 120 Hz.

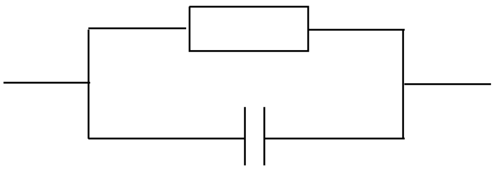

Fig. 5. Equivalent circuit of the impedance (Z) as parallel connected resistance (R) and capacitance (C).

The impedance of the hygrometer is equal to the total impedance of resistance and capacitance connected in parallel (Fig. 5):

$$Z = 1/Y = 1/(1/R + \mathrm{j}2\pi f C), \quad (1)$$

where Y is admittance.

From Figs. 3 and 4, it is seen that a decrease in the calculated impedance of the hygrometer occurs with an increase in the humidity. The impedance–humidity relationship shows that sharp changes cover a wider range of the humidity than the resistive–humidity relationship. This effect plays an important role in the design of the hygrometer based on investigated materials. The impedance depends on both resistance and capacitance changes (Eq. (1)), which is why the impedance–humidity curves are more uniform than those of the resistance and capacitance. As the impedance and resistance decrease simultaneously with humidity, it is obvious that the resistance effect on the impedance is more dominant than the capacitance effect. At frequencies of 120 Hz and 1 kHz, the impedance decreased to 1300 and 425 times respectively in the humidity range of 31%–98%. It was observed that the measured results matched the calculated impedance values. The impedance hygrometer should be used at 120 Hz.

It is known[20] that the value of the capacitance depends on the polarizability of the material. Basically there are several sources: dipolar $\alpha_{\rm dip}$, ionic $\alpha_{\rm i}$ and electronic $\alpha_{\rm e}$ polarizability. In this case the dipolar ($\alpha_{\rm dip}$) polarizability due to the presence of dipoles (H_2O) seems to play a very important role. Electronic polarizability is most universal and arises due to relative displacement of the orbital electrons. As the CuPc may comprise internal charge-transfer complexes and/or external ones with cellulose, we can assume that ionic polarization takes place as well in these organic materials. In Refs. [21–24], the polarizability due to the transfer ($\alpha_{\rm t}$) of charge carriers, such as electrons and holes present at normal conditions in organic semiconductors, was investigated.

The effect of humidity on the hygrometer may be explained in the following way. As the hygrometer is in the humid environment of water molecules, due to differences in the concentration of water molecules in the environment and inside of the bulk of the hygrometer, water molecules diffuse in the bulk of the hygrometer. As water molecules have very high dielectric permittivity compared to cellulose and CuPc, the capacitance of the sensor will actually be changed and controlled by the concentration of water molecules. The water molecules are dipoles, the oxygen atom has a negative charge and hydrogen atoms have positive charges. Because of this the water molecules can play the role of acceptors and can attract electrons from CuPc; as a result, the concentration of holes increases in CuPc (CuPc is a p-type semiconductor) and accordingly decreases the resistance. This was experimentally observed in resistance–humidity relationships. The performance of the impedance humidity sensor depends on proper contribution of the resistive and capacitive components in the impedance. In particular, it affects the shape of the impedance–humidity curve.

To summarize, firstly, the effective (or total) dielectric permittivity of the organic materials increases due to absorption of water molecules which have higher dielectric permittivity than organic materials. Secondly, the decrease of the resistance may be due to the presence of displacement current caused by water molecules. Thirdly, capacitance increases and resistance decreases due to possible doping of the organic material by the water molecules, increase of the polarizability and concentration of charges related to extra charge carriers. These mechanisms are described in detail in Ref. [21]. The obtained data show that the sensitivity of the hygrometer is decreased with increasing frequency. This may be due to comparability of the relaxation time[20] of related processes with the period of applied measuring AC voltage.

An equivalent circuit of the impedance (Z) as parallel connected resistance (R) and capacitance (C) is shown in Fig. 5. The simulation of the impedance–humidity relationship can be easily done by use of Eq. (1) and approaches the simulation of the capacitance, used by our group earlier for organic semiconductor poly-N-epoxypropylcarbazole complex photocapacitive detectors[24].

The obtained data show that resistance and capacitance measurements in the humidity response of the hygrometer are complementary and can be replaced by impedance measurements only. The high sensitivity of the cellulose/CuPc double layer system is due to the high sensitivity of cellulose and CuPc to humidity. The highest sensitivity of the device is also attributed to the surface structure formed by cellulose powder and thin CuPc film.

4. Conclusion

An impedance hygrometer has been fabricated and investigated by using cellulose and copper phtalocyanine (Ag/cellulose/CuPc/Ag). The resistance, capacitance and impedance of the hygrometer were evaluated under the effect of humidity in the range of 31%–98%. It was observed that the capacitance of the sensor increases and resistance and impedance decrease with an increase of the relative humidity. It was found that the impedance–humidity relationship shows more uniform changes in the interval of humidity of 31%–98% compared to the resistance– and capacitance–humidity relationships, which show visible changes in the humidity intervals of 31%–80% and 80%–98% respectively. The impedance hygrometer's performance decreases with an increase of the frequency of measuring AC voltage.

It was observed that the resistance contribution in the impedance is dominant compared to the capacitance. Impedance–humidity measurements only in the case of the Ag/cellulose/CuPc/Ag hygrometer are sufficient for the design of a humidity meter. The humidity-dependent impedance of this sample makes it attractive for use in impedance hygrometers. The impedance hygrometer may be used in instruments for the environmental monitoring and assessment of humidity.

Acknowledgments

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