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Orange Dye Thin Film Electrochemical Hygrometers

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Abstract

Electrochemical hygrometers have been fabricated using orange dye (OD) $C_{17}H_{17}N_5O_2$ thin films, deposited from aqueous solution under normal conditions. The films were deposited on zinc substrates from 10 wt.% solution of OD in distilled water. These films were than used to make samples of Zn/OD-TP/Cu, Zn/OD/Cu and Zn/OD/Graphite (TP stands for tissue paper); copper electrode was used in the form of a mesh and the graphite in the form of a porous solid. Properties of the samples were investigated in a range of 46-78% humidity. Output voltage and current of the sensors were monitored in electrochemical mode of operation, showing a rise of 8 and 100 times, respectively, with an increase in humidity. These electrochemical hygrometers may be potentially useful for developing humidity meters.

Introduction

Literature concerning electronic properties of organic materials has increased rapidly during last few years, for the reason of low cost, simplicity, easiness in fabrication of devices, and interesting electrical properties. Many potential applications of organic semiconductors may be explored by investigation and modifying their conductivity [1-4]. Organic semiconductors have been investigated intensively during the last decade and consequently a variety of sensors were designed and fabricated. Electric properties of some organic semiconductors are very sensitive to humidity, temperature [1,2], IR, visible and UV radiation [5], and different types of gases such as ammonia [6]. Organic material-based transistors that are able to detect charged/uncharged chemical species in aqueous media via the electric field have been described elsewhere [7]. It has been shown that the transistor is sensitive to protons and glucose. A number of ion-sensitive electrode devices, and semi-conducting and electrochemical oxide sensors consisting of liquid and solid electrolyte have been described by someone else [8].

Therefore, research on conductivity of organic semiconductors in different conditions is vital for the development of sensors for humidity, temperature, light, radiation, strain, gases *etc.*

Currently, the most common material used in resistive hygrometers is lithium chloride [9,10]. The mixture of lithium chloride and carbon is placed on an insulating substrate between the metal electrodes, forming a bulk sensor. Resistance of the element decreases with an increase in humidity since more moisture is absorbed by lithium chloride. Resistance of the hygrometer can be measured by applying AC to a Wheatstone bridge or by a combination of current and voltage measurements [9,10]. DC voltages cannot be applied since they tend to break the bond between lithium and chlorine. This resistive hygrometer must be operated at a constant temperature or temperature variation must be compensated. Response times, typically, are of the order of a few seconds [9, 10]. Resistance of hygrometer changes from 10 kΩ to 10^3 MΩ as humidity changes from 100% to 0%.

The orange dye (OD) as a *p*-type organic semiconducting material may potentially be used in electronic and optoelectronic devices. Previously [11], a two-layer structure consisting of poly-N-epoxipropylcarbazole/OD hetero-junction, deposited from solution at high gravity conditions by centrifugation,

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has shown a rectification behavior. On the other hand vapor deposition technology is widely used for fabricating thin film organic devices [1,2]. This low temperature (400-600°C) process allows growing thinner and more uniform films. Practically, it would be more appropriate to deposit thin films by a different method and on a different substrate to fabricate sensor as the properties of the films and sensors depend on fabrication technology. This paper presents the results of investigation on electrical properties of electrochemical hygrometers, fabricated using organic semiconductor orange dye films deposited at normal conditions.

Experimental

Commercially available organic semiconductor orange dye (OD) $C_{17}H_{17}N_5O_2$ (Fig. 1) with molecular weight 323 and density of 0.9 g/cm^3, was used for fabrication of electrochemical hygrometer. It was confirmed by "hot-probe" method that the material was a *p*-type semiconductor. Zinc and copper (or graphite) were selected as electrodes for electrochemical hygrometer because of their large difference in standard electrode potentials [12]. Samples were prepared by depositing thin films of OD from 10 wt.% aqueous solutions by drop coating, on zinc substrates at normal temperature and pressure. These samples were used in fabricating three types of electrochemical hygrometers: Zn/OD-TP/Cu, Zn/OD/Cu and Zn/OD/Graphite (TP is tissue paper); copper electrode was used in the form of mesh and the graphite electrode was a porous solid. In the Zn/OD-TP/Cu hygrometer the tissue paper was put on zinc substrate and wetted by a drop of OD solution. In the case of Zn/OD/Cu and Zn/OD/Graphite hygrometers, the OD solution was directly deposited on zinc substrate.

The samples were dried at room temperature in 3-4 hrs. Although the samples were of sandwich-type, the net-metal electrode or porous graphite allowed the moisture to penetrate through them to the OD film. The size of the OD film on the zinc substrate was 20×10 mm and the thickness was 0.1 mm (it was estimated using the parameters such as mass, area and density of the deposited matter). In [13] the OD films deposited from solution were investigated by scanning electron microscope. It was found that the films have mosaic structure. The output voltage and current in the electrochemical cells formed by the samples were measured at room temperature in a humidity range of 46-78%, by conventional digital volt and ampere meters with an error of ±2%. In all the investigated hygrometers, polarity of generated voltage on zinc electrode with respect to copper or graphite was negative. Response and relaxation times at measurement of sensor's voltage and currents was in the range of 3-10 sec. The samples showed stability and reproducibility of the electric properties. The relative humidity was measured with an error of ±3% by conventional digital meter.

Results and Discussion

Current-humidity relationship of three electrochemical hygrometers is shown in Fig. 2. Within the measured range of humidity, the average currents of the hygrometers Zn/OD-TP/Cu, Zn/OD/Cu and Zn/OD/Graphite have been found to increase by 94, 27 and 99 times, respectively. Figure 3 shows voltage-humidity relationships; the voltages of Zn/OD-TP/Cu, Zn/OD/Cu and Zn/OD/Graphite have increased by 1.5, 3.2 and 8 times respectively.

In Figure 3 the voltage shown on Cu or graphite electrodes with respect of Zn electrode. Experimental data show that sensitivity of hygrometers based on the OD to humidity is substantially large and this material may be used in humidity meters just as lithium chloride [9,10]. Table 1 shows average humidity-current and humidity-voltage coefficients of orange dye electrochemical hygrometers. It was observed that Zn/OD-TP/Cu and Zn/OD/Graphite hygrometers had high sensitivity for current toward humidity; and the Zn/OD/Graphite and Zn/OD/Cu are more sensitive towards voltage.

The humidity relationships of the hygrometers parameters are nonlinear, but may be corrected by linearization circuit that is normally used in instrumentati-

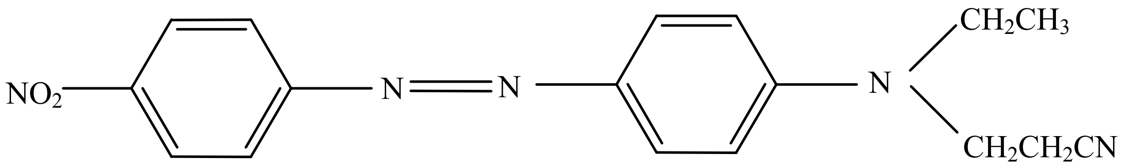

Fig. 1. Molecular structure of orange dye (OD).

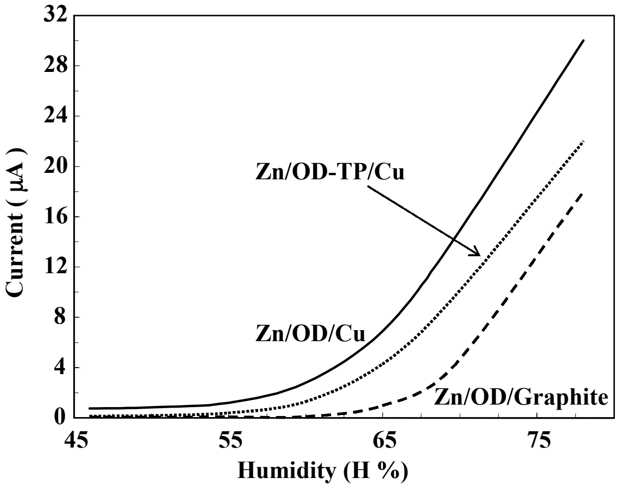

Fig. 2. Current-humidity relationship of the Zn/OD-TP/Cu (1), Zn/OD/Cu (2) and Zn/OD/Graphite (3) electrochemical hygrometers.

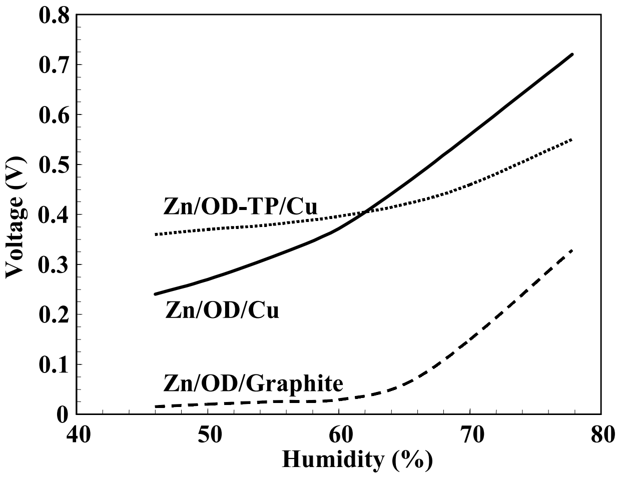

Fig. 3. Voltage-humidity relationship of the Zn/OD-TP/Cu (1), Zn/OD/Cu (2) and Zn/OD/Graphite (3) electrochemical hygrometers.

Table 1

Effect of humidity on current and voltage of various hygrometers

Series #	Hygrometer system	$\frac{\Delta I\ 100\%}{I\ \Delta H\%}$	$\frac{\Delta V\ 100\%}{V\ \Delta H\%}$
Series 1	Zn/OD-TP/Cu	360	2
Series 2	Zn/OD/Cu	105	8
Series 3	Zn/OD/Graphite	360	25

on devices with nonlinear sensors. The presence of electrochemical effect (generation of voltage and current due to humidity in the samples) is probably related to the presence of mobile ions in OD-H_2O medium.

Large increase of the sensors current with humidity may be, first of all, due to the rise of the OD conductivity or ionic conduction. It is known that ionic conduction depends on dielectric constant of the medium [14]. The absorption of water, which has a relatively high dielectric constant, may generally enhance the ionic conduction and, consequently the electrochemical effect in Metal-OD-Metal system. The following electrochemical phenomenon seems to be most appropriate at this stage: highly mobile π-electrons of the OD molecules correlate with water molecules resulting in an increase of ion concentration in OD-H_2O system. However, further investigations are required to highlight the reasons of the phenomenon.

Conclusion

Electrochemical hygrometers consisting of organic semiconductor dye ($C_{17}H_{17}N_5O_2$) films deposited from aqueous solutions have been locally fabricated, and their properties have been investigated. It was found that hygrometers with Zn/OD-TP/Cu (TP: tissue paper) and Zn/OD/Graphite systems exhibited higher sensitivity for current and Zn/OD/Graphite and Zn/OD/Cu system for voltage as well. The hygrometers may be used for development and fabrication of humidity meters.

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