PHTHALOCYANINE HYBRID HUMIDITY SENSORS BASED ON CARBON NANOPARTICLES AND SUBSTITUTED PHTHALOCYANINES

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Abstract

New type of humidity sensor based on Carbon thin film active nano layers, modified with sodium salt of sulfonated Nickel phthalocyanine is presented. The sensor shows high sensitivity due to the high surface area of Carbon nanoparticles, good long-time stability and sensitivity in the range from 20 to 85 \% relative humidity (RH). The response is linear in semilogarithmic plot – logarithm of impedance vs. RH and fully reversible.

1. INTRODUCTION

Over many years humidity sensors have attracted considerable attention of engineers due to their useful applications in industry and environmental monitoring. [1, 2]. Sensors based on Al\textsubscript{2}O\textsubscript{3} are very often used [3]. Cheap humidity sensors are often based on thin films of polymers consisting of saturated main chains and ionizable side groups [4, 5]. Sensitivity to humidity is based on the dissociation of side groups of the type A\textsuperscript{+}B\textsuperscript{-}, e.g., COO\textsuperscript{-}Na\textsuperscript{+} and SO\textsubscript{3}\textsuperscript{-}Na\textsuperscript{+}. The films can be prepared by cold technologies, like spin coating polymer solutions, casting, doctor blading, etc. Sensors based on ceramics have often an insufficient sensitivity over wide humidity range, bad reversibility, drifts in base resistance due to the chemisorption of water molecules, etc. Our interest is the developing of fast and sensitive humidity sensors based on derivatives of phthalocyanine. We described the humidity sensor based on TiO\textsubscript{2} nanolayer modified with sulfonated hydroxyaluminium phthalocyanine [6]. We also developed a new humidity sensor sensitive over wide humidity range (20 – 90\% RH), based on active layer of sulfonated Nickel phthalocyanine (NiPcS), covered with the protective layer of sulfonamidic nickel phthalocyanine [7]. Recently we have developed new types of double layers humidity sensors based on Carbon nanoparticles and sulfonated derivatives of Nickel phthalocyanine (NiPcS). The idea was based on the fabrication of sensors with nanolayers of Carbon nanoparticles modified with NiPcS, which is located either beneath the carbon layer or on the surface of it.

2. EXPERIMENTAL

2.1. Materials

2.1.1. Sodium salt of sulfonated Nickel phthalocyanine

Sulfonated Nickel phthalocyanine (Ni)Pc(SO\textsubscript{3}H)\textsubscript{x} was synthesized in the way as described. Its chemical structure is shown in Scheme 1. The material used in this work consisted mainly of mono- (x = 1) di- (x = 2) and tri- (x = 3) sulfonated molecules.
Scheme 1. Sulfonated Nickel phthalocyanine, NiPc(SO$_3$H)$_x$, $x = 1 - 4$

(Ni)Pc(SO$_3$H) was synthesized from Nickel phthalocyanine (Ni)Pc. The sulfonation process was carried out in a four necked glass flask, which was heated in an oil bath, equipped with reflux cooler, agitator, thermometer and dosing funnel. 200 g of fuming sulfuric acid (5%) was charged into the flask and subsequently 20 g of (Ni)Pc was gradually charged through the dosing funnel into the agitated fuming sulfuric acid. The mixture was agitated at 30 °C until all (Ni)Pc was fully dissolved. After that the dosing funnel was removed and the inlet of nitrogen was installed instead of it. The process of sulfonation was then carried out under the nitrogen blanket. The reaction mixture was agitated and heated up to temperature 115 °C and subsequently kept for 30 minutes at the adjusted temperature. After the finishing of the sulfonation process, the reaction mixture was slowly cooled down to laboratory temperature and subsequently charged with a dropping funnel into the vigorously agitated mixture consisting of 2000 g of ice and 1000 g of water. The water suspension was then filtered with a Büchner funnel, the filter cake was washed with distilled water until no sulfate anions were detectable in the filtrate. Thoroughly washed filter cake of sulfonated (Ni)Pc was dispersed in distilled water and pH was adjusted to pH 11 using 10% solution of NaOH. In this way a sodium salt (NiPcS in further text) was prepared. The solution obtained in this way was dried in rotary laboratory vacuum evaporator. The product, NiPcS, contained 13.0 % mono, 61.6 % di, 23.5 % tri and 1.9 % tetra sulfonated species according to HPLC analysis.

2.1.2. Thin Carbon films preparation

The carbon film was applied on the substrate by the method of physical vapour deposition (PVD). To ensure the reproducibility of mechanical and electrical parameters of the carbon layer, the following procedure was applied: The basic substrate was cleaned in ultrasonic bath and dried. After that the substrate was placed into a vacuum chamber of Carbon sputtering machine. The chamber was then evacuated and filled by argon for three times. The pressure after the last cycle was around 4x10$^{-2}$ mbar. The carbon layer was deposited on the substrate by PVD method at 6 V. DC current flowing through the carbon rod, which was situated above the substrates, was 150 A. The thickness of the carbon layer was controlled by deposition time. After 1 s deposition the layer was 6 nm thick, after 2 s deposition 11 nm thick. The substrate covered with one carbon layers without NiPcS was used as control unit of humidity sensitivity.
2.1.3 Double layer NiPcS/Carbon humidity sensors

The humidity sensor was prepared on ceramic substrate, containing 99% of alumina, with interdigital Au electrodes having isolation gaps 25 µm wide. The electrodes were made by lift off method. This method is based on cold sputtering of metal in vacuum on the substrate with photoresist pattern. Electrodes were made by the sequential deposition of Au layers. The thickness of the electrodes was about 400 nm. Two methods were used for the preparation of double layer NiPcS/Carbon humidity sensors.

(i) Sodium salt of sulfonated Nickel phthalocyanine (NiPcS) was deposited on the substrate with interdigital electrodes from water solution by spin-coating. The rotation speed of spin-coater was 3000 rpm. Subsequently the NiPcS layer was covered by carbon nano layer, 6 nm thick by the PVD method described above (sensor NP-C-2T).

(ii) NiPcS layer was deposited by spin-coating water solution on carbon nano layer (6 or 11 nm thick) covering the interdigital electrode system on the substrate (sensors C-NP-1T and C-NP-1S). The substrate covered with one carbon layer 6 nm without NiPcS was used as control unit of humidity sensitivity (sensor CT1).

Table 1 illustrates prepared and measured humidity sensors.

### Table 1: Humidity sensors used for testing in climatic chamber

<table>
<thead>
<tr>
<th>Sensor number</th>
<th>Components</th>
<th>Structure</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>CT1</td>
<td>C only</td>
<td>C layer only</td>
<td>C layer 6 nm thick</td>
</tr>
<tr>
<td>C-NP-1T</td>
<td>NiPc +C</td>
<td>NiPc on C layer</td>
<td>C layer 6 nm thick</td>
</tr>
<tr>
<td>C-NP-1S</td>
<td>NiPc +C</td>
<td>NiPc on C layer</td>
<td>C layer 11 nm thick</td>
</tr>
<tr>
<td>NP-C-2T</td>
<td>NiPc +C</td>
<td>C layer on NiPc</td>
<td>C layer 6 nm thick</td>
</tr>
</tbody>
</table>

2.2. Measurement of sensor characteristics

The measurements of properties of double layer NiPcS/C humidity sensors and reference sensor mentioned in Table 1 were carried out in a climatic chamber with controlled temperature and humidity. The measurements were fully automatic in humidity and temperature ranges from 20 to 90% RH and from 20 to 50 °C, respectively. Humidity was increased stepwise, 0.5% RH per min. The measurement cycle is shown in Figure 1.
Figure 1: Humidity and temperature cycles during the measurements

Electrical parameters of samples were measured by RLC bridge Agilent E4980A. The results of the measurements are shown in Figures 2 - 5

Figure 2. Humidity dependence of impedance of reference humidity sensor CT1 (nano layer 6 nm)

Figure 3. Humidity dependence of impedance of humidity sensor C-NP-1T (C nano layer 6 nm on interdigital electrodes, NiPcS fixed on C surface)

Figure 4. Humidity dependence of impedance of humidity sensor C-NP-1S (C nano layer 11 nm on interdigital electrodes, NiPcS fixed on C surface)

Figure 5. Humidity dependence of impedance of humidity sensor NP-C-2T (NiPc layer on interdigital electrodes, C nanolayer 6 nm fixed on the surface of NiPcS layer)
Stability test was performed using the cycles 30 °C / 30% RH | 85 °C / 85% RH, water resistance test by dipping of the sensor to water. The results of the measurements are presented in Fig. 6 and 7.

![Figure 6. Long time stability and reversibility tests of impedance of humidity sensor C-NP-1T (C nano layer 6 nm on interdigital electrodes, NiPcS fixed on C surface)](image)

![Figure 7. Time dependence of impedance of humidity sensor dipped to the water. NiPc (only NiPcS layer without C nanolayer on the surface of interdigital electrodes, blue curve), CNiPc (C nanolayer of 6 nm on surface of interdigital electrodes with NiPcS on C surface violet curve)](image)

3. RESULTS AND DISCUSSION

From the humidity dependence of impedance of the reference humidity sensor CT1 (see Figure 2) it is clear, that the carbon nanolayer itself (without NiPcS) cannot be used as a humidity sensor because the impedance is not sensitive to humidity in the range from 20 to 60% RH. When NiPcS is present the sensors are well sensitive to humidity, cf. Figures 3–5. The response follows from the dissociation of SO₃Na groups.

A tendency to saturation at low relative humidity was also observed on sample C-NP-1S, composed of 11 nm C nano layer deposited on interdigital electrodes and NiPcS layer fixed on the surface of the C nanolayer (see Figure 4). The low-humidity saturation limits the use of this sensor in technical practice. The saturation is very probably influenced by low conductivity of carbon nanolayer at low humidity. The saturation effect is limited if carbon layer is thinner, cf. Figure 3 (humidity sensor C-NP-1T, composed of carbon nanolayer of 6 nm deposited directly on interdigital electrodes with NiPcS fixed on its surface). Similar impedance vs. humidity dependence was observed in the case when NiPcS was directly deposited on the electrode system and C nanolayer 6 nm is fixed on the surface of NiPcS layer - sensor NP-C-2T (see Figure 5). Thus, the sensors of the type C-NP-1T and NP-C-2T are recommended for further development. Besides, the humidity sensor C-NP-1T shows good long time stability (see Figure 6) and stability to direct water contact (see Figure 7). Its stability to water was three times higher than that of NiPcS layer directly deposited on Au interdigital electrodes.
4. CONCLUSION

Hybrid double layer humidity sensors based on carbon nanolayer and the layer of sodium salt of sulfonated Nickel phthalocyanine (NiPcS) were studied. They show good response to humidity in the range from 20 to 90 % RH. Humidity sensor prepared from carbon nanolayer without NiPcS was not sensitive to water in the range from 20 to 60 % RH.

C-NP-1S sensor, composed of 11 nm C nanolayer deposited on interdigital electrodes and NiPcS layer fixed on it, shows response saturation at low humidity which limits its use in technical practice.

Sensor C-NP-1T, composed of 6 nm carbon nanolayer deposited on interdigital electrodes and NiPcS layer fixed on it shows good response to humidity and is recommended for further development.

Similarly behaves sensor NP-C-2T of the type: interdigital electrodes | NiPcS | carbon nanolayer.

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