HUMIDITY SENSOR BASED ON TiO₂ NANOPARTICLES AND SODIUM SALT OF SULFONATED AIOH PHTHALOCYANINE

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Abstract

New type of humidity sensor based on TiO₂ nanoparticles and sodium salt of sulfonated AIOH phthalocyanine is presented. The sensor shows high sensitivity due to the high surface area of TiO₂ nanoparticles, good long-time stability and sensitivity in the range from 20 to 80 % RH. The response is linear in semilogarithmic plot – logarithm of impedance vs. RH and fully reversible.

1. INTRODUCTION

Humidity sensors have attracted considerable attention of engineers due to their useful applications in industry and environmental monitoring [1,2]. Sensors based on Al₂O₃ are very often used [3]. Cheap humidity sensors are often based on thin films of polymers consisting of saturated main chains and ionizable groups [4,5]. Sensitivity to humidity is based on the dissociation of side groups of the type A⁺B⁻, e.g., COO⁻Na⁺ and SO₃⁻Na⁺. The films can be prepared by cold technologies, like spin coating polymer solutions, casting, doctor blading, etc. Another group of polymers with sensitivity to humidity represent conjugated polymers. However, both groups of the polymers often show low temperature and humidity stability. Many commercially available humidity sensors are based on ceramic materials [6-8] due to low cost and quite good performance. They offer major advantages with high resistance to chemical attack, thermal stability and mechanical strength. However, some problems can be mentioned, like insufficient sensitivity over wide humidity range in some types of sensing elements, reversibility and drift in base line with time due to the chemisorption of various gasses.

To improve the sensitivity nanoscale structures can be used. As a typical example we can mention thin layers prepared from TiO₂ nanoparticles which are characterized by sufficient sensitivity for many applications. The sensitivity to other vapors than water can be limited by hydrophilic layer coverage. It has been expected that this structure would have adequate sensitivity to water vapors and limited sensitivity to other gas molecules. This type of the humidity sensors is presented in this paper. Sodium salt of sulfonated AIOH phthalocyanine was used as a covering layer.
2. EXPERIMENTAL

2.1. Materials

TiO₂ nanoparticles were applied in the form of paste (Solaronix, Switzerland, Type: HT/SP). Sodium salt of sulfonated AlOH phthalocyanine, \((\text{AlOH})\text{Pc}(\text{SO}_3\text{Na})_x\) [AlPcS in further text] was synthesized in the way described below. Its chemical structure is shown in Scheme 1. The material used in this work consisted mainly of di- \((x = 2)\) and tri- \((x = 3)\) sulfonated molecules.

![Scheme 1. Sodium salt of sulfonated AlOH phthalocyanine AlPcS](image)

AlPcS was synthesized from hydroxyaluminium phthalocyanine \((\text{AlOH})\text{Pc}\). The sulfonation process was carried out in the four necked glass flask, which was heated in an oil bath, equipped with reflux cooler, agitator, thermometer and dosing funnel. 300 g of fuming sulfuric acid was charged into the flask and subsequently 30 g of \((\text{AlOH})\text{Pc}\) was gradually charged through the dosing funnel into the agitated fuming sulfuric acid. The mixture was agitated at 30 °C until all the \((\text{AlOH})\text{Pc}\) was fully dissolved. After that the dosing funnel was removed and an 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 from 115 to 125 °C and subsequently kept for 30 minutes at the adjusted temperature. The concentration of fuming sulfuric acid and the temperature of the sulfonation were chosen according to the target level of the sulfonation. The lower sulfonated \((\text{AlOH})\text{Pc}(\text{SO}_3\text{H})_{1-2}\), mostly mono- and di-sulfonated ones, were obtained when 5 % fuming sulfuric acid was used at the temperature of 115 °C; the contents of mono-sulfonated and di-sulfonated \((\text{AlOH})\text{Pcs}\), as determined by high pressure liquid chromatography (HPLC), were 35,7 and 53,0 %, respectively. The higher sulfonated \((\text{AlOH})\text{Pcs}\), mostly di- and tri-sulfonated, were obtained when 6 % fuming sulfuric acid was used at the temperature of 125 °C. The contents of di-sulfonated and tri-sulfonated AlPcS, as determined by HPLC, were 28,3 and 54,5 %, respectively.

After the finishing of the sulfonation process, the reaction mixture was slowly cooled down to the laboratory temperature and subsequently charged with a dropping funnel into the vigorously agitated mixture of 2000 g of ice and 1000 g of water. The water suspension was then filtered with a Buchner funnel, the filter cake was washed with distilled water until no sulfate anions were detectable in the filtrate. Thoroughly washed filter cake of sulfonated \((\text{AlOH})\text{Pcs}\) was dried in laboratory dryer at the temperature of 105 °C until the constant weight. The contents of particular sulfonated \((\text{AlOH})\text{Pcs}\) were determined by HPLC. The dry product of \((\text{AlOH})\text{Pc}\) sulfonation was always a mixture of mono-, di-, tri- and tetra-sulfonated moieties; no changes in the conditions of the sulfonation process were not able to control the process in such a way, to get the...
particular sulpho-derivatives as pure products. In order to prepare quasi-pure mono-, di-, tri- and tetra-sulfonated (AlOH)Pc(SO$_3$H) the mixtures of sulphonated derivatives, prepared by the above described processes, were separated by column liquid chromatography, the purity of each dry product was determined by HPLC method.

2.2. Thin films preparation

Thin films of TiO$_2$ were prepared from the paste by screen printing on glazed ceramic substrates with gold interdigital electrodes (electrode gap was 50 µm). After the deposition the layers were annealed at 450 °C, 60 min. The microscopic image of TiO$_2$ layer (laser confocal mode magnification 7200×) is shown in Fig. 1. Then, AlPcS was deposited from a water solution by dipping (concentration 200 mg AlPcS per 1 l of water) for 60 min and dried at 80 °C. Note, the higher annealing temperatures (up to 500 °C) and longer annealing time (up to 12 h) did not influence the sensor properties too much.

![Microscopic image of TiO$_2$ layer](image)

**Fig. 1.** Microscopic image of TiO$_2$ layer – Solaronix HT/SP paste, magnification 7200 times, laser confocal mode.

2.3. Response detection

The response on humidity exposure was monitored by means of impedance change and detected as the change of frequency (f) obtained in impedance-frequency converter.

3. RESULTS AND DISCUSSION

The aim of this work was to improve the sensitivity and stability of humidity sensor with high surface area based on the layer of TiO$_2$ nanoparticles.

The dependences of the frequency (f) on relative humidity (RH) are shown in Fig. 2. From the figure it follows that TiO$_2$ layer seems to be good humidity sensor, linear in the semilogarithmic plot of log f vs. RH (curve 2). However, the response of the sensor is not constant in long time due to the sorption of various pollutants from environment as it follows from Fig. 3, cycles set 2, full line. We were not able to compensate this drift.
Thus, the TiO$_2$ layer was modified by phthalocyanine AlPcS. It must be noted that AlPcS alone is not suitable for the sensor fabrication, as follows from Fig. 2, curve 3:

(i) The course of the log $f$ vs. RH dependence was not linear and frequency shows a saturation for humidities higher than about 50 % RH.

(ii) The film is not stable at higher humidities and is washed out from the electrode system due to its water solubility.

The advantage of the hybrid sensor is that the responses are stable in time as it follows from Fig. 3, cycles set 1, dashed line. The dependence of the log $f$ vs. RH of the TiO$_2$ with adsorbed AlPcS is shown in Fig. 2, curve 1: The response is linear in log $f$ vs. RH coordinates. The weak sublinearity above 75 % RH does not influence the accuracy of the humidity detection too much. The device sensitivity $S = \Delta \ln f / \Delta$ RH ($f$ in Hz and RH in %) was increased from $S = 0.087$ to $S = 0.19$.

**Fig. 2.** The dependences of the detection frequency on relative. Curve 1 – layer TiO$_2$ annealed at 450 °C for 60 min with adsorbed phthalocyanine AlPcS; curve 2 – TiO$_2$ layer annealed at 450 °C for 60 min; curve 3 – film of AlPcS.

**Fig. 3.** The dependences of the detection frequencies on time at 40 °C. Testing cycle consists of a stepwise humidity change to and from 20 and 90 % RH in about 2 % RH steps. The courses in the plot illustrate the behavior of the three types of sensor during six cycles. Cycles set 1 – layer TiO$_2$ annealed at 450 °C for 60 min with adsorbed phthalocyanine AlPcS; cycles set 2 – TiO$_2$ layer annealed at 450 °C for 60 min; cycles set 3 – film of AlPcS.

AlPcS is very stable organic compound. The substitution with $SO_3$Na groups makes it hydrophilic. The ability of the substituent to dissociate results in the improved electrical (ionic) conductivity. It allows to increase the sensitivity of TiO$_2$ layer to humidity.
4. CONCLUSION

TiO₂ represents a good material for humidity sensors. The sensitivity can be improved by the increase of surface area by using nanoparticles. However, these humidity sensors are not stable in time. This disadvantage was diminished by the AlPcS adsorption.

To summarize: TiO₂ layers prepared from the Solaronix paste with adsorbed phthalocyanine AlPcS show good stability and sensitivity to humidity in the range from 20 to 80 % RH. The long-time stability is very good. The response is linear in semilogarithmic plot – logarithm of detection frequency vs. RH and fully reversible which introduces a good background for the humidity sensors fabrication.

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