



A novel concept for humidity compensated sub-ppm ammonia detection

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ABSTRACT

We report on the principle of a discriminative sensor for the detection of ammonia gas at varying levels of humidity. This is achieved by using two differently conducting formulations of poly(styrene sulfonate) doped poly(3,4-ethylenedioxythiophene) (PEDOT/PSS) in two sensor elements. Humidity and ammonia concentration can be separated because the sensor elements show opposite response to the two stimuli: contact to ammonia leads to an increase in the electrical resistivity of both formulations, while a change in the surrounding humidity level decreases the resistivity of one of the PEDOT/PSS types, while it increases that of the other. Moreover, it is shown that with the hereby presented discriminative sensor concept ammonia concentrations in the sub-ppm regime can be detected.

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1. Introduction

Conducting polymers such as polypyrrole, polythiophene, polyaniline (PANI) and poly(3,4-ethylenedioxythiophene) (PEDOT) are widely used as the active materials in the field of organic sensors [1–3]. There, the most common type of sensor is the so-called chemiresistor, where the resistivity of a conducting polymer is sensitive to an analyte gas [1]. The active material of such a device can generally be applied by spin- or drop-casting and for some of the previously mentioned materials also by various printing techniques, like inkjet printing [4,5]. The advantage of such sensors is that they can be fully integrated into flexible electronic circuits, like flexible radio-frequency identification (RFID) tags. Furthermore, a high sensitivity and good response time towards basic gases, including ammonia, can be achieved [1,6–8], which makes them perfect candidates for low-cost and even disposable sensor tags. The measurement of the ammonia concentration has applications in the agricultural sector [9], in clinical diagnosis or environmental monitoring [8]. For measuring the ammonia concentration to monitor the freshness or spoilage of food [10,11]. The sensors need to be

cheap, small and capable of being easily integrated into RFID tags [12], the requirements regarding their response-times are, however, usually not particularly tight.

Unfortunately, there is also a big shortcoming of sensors using conducting polymers, which up to date inhibits their use in practical applications. This is the fact that their electrical resistance is strongly affected by coexisting gases, different from the objective gas which leads to a low selectivity towards different analytes [3]. One well known cross-sensitivity is caused by the interaction with water vapour [13,14]. For PEDOT/PSS such water exposure can influence the resistivity due to a change of the work function [15], due to ionic contributions [16] and due to a change in the morphology [17]. The sensor element then cannot distinguish, whether the observed resistivity change is caused by a change in the surrounding humidity level or by a change in the analyte concentration.

2. Experimental

In this study, we focus on chemiresistors made of poly(styrene sulfonate/sulfonic acid) doped poly(3,4-ethylenedioxythiophene) (PEDOT/PSS), a classical hole transporting electrode material used in organic electronics. Two different formulations of PEDOT/PSS with intrinsically different resistivity levels are used to simultaneously detect changes in the humidity level and in the ammonia

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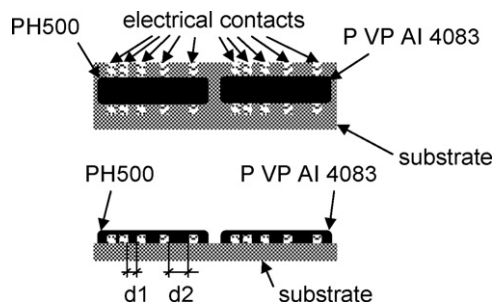


Fig. 1. Schematic setup of two sensor elements with the two PEDOT/PSS formulations, top-view (upper part) and cross-section (lower part). Shown is the substrate with the electric contacts and the two layers of PEDOT/PSS (Baytron PH 500 and Baytron P VP Al 4083). The conduction path lengths between adjacent electric contacts (0.3, 0.5, 1.0 and 1.5 mm) are schematically shown (d1 and d2).

concentration. The used materials are commercially available under the trademark of Baytron PH 500 and Baytron P VP Al 4083.¹ Both materials are obtained in aqueous dispersion. The formulation of PH 500 is a homogenized version with small particle size, which is specifically tailored to show high conductivity (as needed for conductive coatings or anti-static coatings, with a minimum specific conductivity of 300 S/cm after addition of 5% dimethyl sulfoxide [18]), while the material P VP Al 4083 has a much lower conductivity (with a resistivity of 500–5000 Ω cm according to the manufacturers datasheet [19], corresponding to a specific conductivity of 0.002–0.0002 S/cm). This is because it is designed for the integration as a hole-injection layer in organic light emitting diodes.² All sensor materials in this study were applied via drop-casting, using a Finnipipette and approx. 50 μ l PEDOT/PSS, onto a printed-circuit board (PCB) with pre-structured NiAg coated Cu contact pads. About 12 devices for each of the two used materials are obtained with different conduction path lengths of 0.3, 0.5, 1.0 and 1.5 mm (see schematic setup in Fig. 1). The electrical resistance of the sensor elements are consecutively measured by the two point-probe method (applying a DC voltage), using a Keithley 2701 digital multi-meter with two automated switch cards (Keithley 7702 and 7708). The whole sensor array is exposed to a streaming carrier gas, which is either dry or humidified argon (Linde Gas, 5.0 purity) or dry or humidified laboratory air. Humidification is achieved by letting the gas through a bubbler filled with distilled water. The dry or humidified carrier gas is then mixed with pure ammonia gas (Linde Gas, 4.5 purity) or a gas mixture of 100 ppm ammonia in argon (custom-made by Linde Gas). To achieve the target ammonia concentration, we used two rotary flow meter (Krohne DK 800; 0–100 l/h for Ar 0–10 l/h for ammonia; the different densities of the Ar/ammonia custom-made mixture has been accounted for using the data sheets provided by Krohne). The obtained flow values are given below when discussing the individual experiments. The relative humidity (RH) is measured at the beginning and at the end of each measurement using a VOLT CRAFT HT-200 temperature and humidity sensor. When switching from dry to humidified carrier gas, the relative humidity inside the sample takes a certain time to reach a constant value. Prior to that, the resistivity response overshoots the stable values reached after equilibration. This is primarily a consequence of significantly increased humidity levels right after starting to pass the carrier gas through the bubbler (i.e., a complication of our measurement setup). For

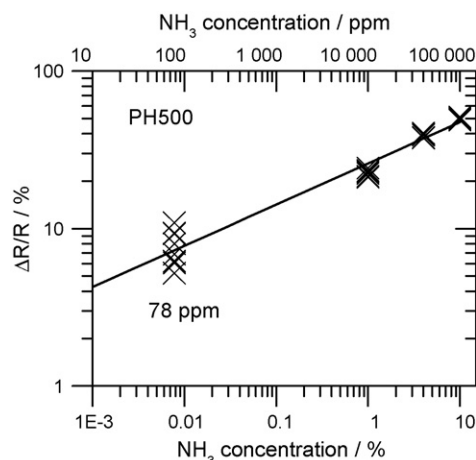


Fig. 2. Log-log plot of the relative change of resistance of the sensor element with Baytron PH 500 as a function of the ammonia concentration, using pure Ar as carrier gas.

Baytron P VP Al 4083, where a resistivity decrease is observed in humid environments, also an additional time-dependent ionic contribution to current flow cannot be excluded at early stages of the experiment, as it has been reported in Ref. [20] at high relative humidity levels. To prevent any of these effects from interfering with our measurements, in the following only data are reported that have been obtained under operating conditions in which time-dependent contributions to the humidity induced resistivity changes have subsided. The temperature during all measurements was $(25 \pm 2)^\circ\text{C}$.

3. Results and discussion

The sensor element responds to different concentrations of ammonia by an increase of its resistance. The relative change of the resistance of nine exemplary sensor elements (2 elements with channel length of 0.3, 0.5 and 1.5 mm respectively, and 3 elements with a channel length of 1.5 mm) are shown in Fig. 2 (with the material PH 500 using dry Ar as carrier gas). It can be seen from the responses of these 9 different sensor elements that the relative change of the resistivity is $(50 \pm 1)\%$ at 10% NH_3 concentration $(39 \pm 1)\%$ at 4% NH_3 concentration $(23 \pm 1)\%$ at 1% NH_3 concentration and $(8 \pm 2)\%$ at 78 ppm NH_3 concentration. The influence of the contact resistance is minor, as no dependence of the channel length was observed. Overall, we find a linear response in a log-log plot over a wide concentration range (cf., Ref. [5]).

For practical applications the regime of very low ammonia concentrations is of high importance. In real situations these low ammonia concentrations must be measured under conditions where other coexisting gases (such as oxygen, nitrogen and humidity) are present. In the following paragraphs it will be demonstrated that a reproducible response can be achieved at ultra-low ammonia concentrations in the sub-ppm level in ambient gas-surroundings [21].

An exemplary measurement of the electrical resistances of the sensor elements with the two materials PH 500 and P VP Al 4083 is shown in Fig. 3. The measurement takes place in a carrier gas of moderately humidified argon (at a relative humidity of 12.5%) and is shown after an equilibration phase. For 10 min a small amount of dry ammonia gas is mixed with the carrier gas, at a concentration of 0.7 ppm ammonia (by setting the flow rate for argon to 100 l/h and for the gas mixture of 100 ppm ammonia in argon to 0.7 l/h). In both sensor elements a clear increase of the electrical resistance is observed during exposure to ammonia, due

¹ The same materials are now available under the new trademark CLEVIOS PH 500 and CLEVIOS P VP Al 4083. For details of the used materials see www.baytron.com or www.clevios.com.

² The conductivity has to be low for this application because a low cross-talk between adjacent pixels is needed.

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