A novel concept for humidity compensated sub ppm ammonia detection

Peter Pacher[a,*], Alexandra Lex[b], Sabrina Eder[a], Gregor Trimmel[b], Christian Slugovc[b], Emil J. W. List[a,c] and Egbert Zojer[a,**]

a) Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz (Austria)

b) Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 16, A-8010 Graz (Austria)

c) NanoTecCenter Weiz Forschungsgesellschaft mbH, Franz-Pichler-Straße 32, A-8160 Weiz (Austria)

*) E-mail: pacherpeter@gmail.com

**) Corresponding author: Tel: ++433168475 Fax: : ++43316108475

E-mail: egbert.zojer@tugraz.at

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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-ethylenedioythiophene) (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.

1. Introduction

Conducting polymers such as polypyrrole, polythiophene, polyaniline (PANI) and poly(3,4-ethylenedioythiophene) (PEDOT) are widely used as the active materials in the field of organic sensors [1,2,3]. 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, such as 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 tags (RFID). Furthermore, a high sensitivity and good response time towards basic gases, including ammonia, can be achieved [1,6,7,8], 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 caused by 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 can not 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-ethylenedioythiophene) (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 concentration. The used materials are commercially available under the trademark of Baytron PH 500 and Baytron P VP AI 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% dimethylsulfoxyd [18]), while the material P VP AI 4083 has a much lower conductivity (with a resistivity of 500 to 5000 Ohm cm according to the manufacturers datasheet [19], corresponding to a specific conductivity of 0.002 to 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 µl 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**).

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[1] The same materials are now available under the new trademark CLEVIOS PH 500 and CLEVIOS P VP AI 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.

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 density 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 VOLTCRAFT 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 as through the bubbler (i.e., a complication of our measurement set-up). For Baytron P VP AI 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±2)°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 mm, 0.5 mm and 1.5 mm respectiveley, and 3 elements with a channel length of 1.5 mm) in dry Ar are shown in **Fig. 2** (with the material PH 500 in a gas surrounding of pure and dry Argon gas). It can be seen from the responses of these 9 different sensor elements that the relative change of the resistivity is (50±1)% at 10% NH_3 concentration, (39±1)% at 4% NH_3 concentration, (23±1)% at 1% NH_3 concentration and (8±2)% at 78ppm NH_3 concentration. The influence of the conatct 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 containing humidity [21].

An exemplary measurement of the electrical resistances of the sensor elements with the two materials PH 500 and P VP AI 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 ten minutes 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 to the earlier mentioned de-doping process [1]. I.e., the increased hole concentration in PEDOT caused by acid doping stabilized by PSS is compensated by the ammonia acting as a base in analogy to what we have observed for hole-conducting organic thin-film transistors with poly(thiophene) active layers interface doped in the channel region by sulfonic-acid bearing self-assembled monolayers.[22] After turning off the ammonia and purging the device for ten minutes with pure argon, the electrical resistance nearly restores to the value observed at the beginning of this first measurement cycle. In a second equivalent measurement cycle the same qualitative behaviour is observed.

It can also be seen in Fig. 3 that the electrical response has not yet reached a steady value after the ten minutes of measurement time. Due to this long response time, the real base value for the resistance is not reached in this experiment.

The long response time is attributed to the diffusion process of the analyte into the organic sensing layer, and thus depends on the concentration gradient. Nevertheless, most applications targeted by this sensor concept are not time critical, as the observed underlying process (such as the spoilage of food) is much slower than the response time of this sensor.

The situation is different upon exposure of the two devices to ammonia at different levels of relative humidity, as shown in Fig. 4. In this experiment compressed laboratory air is used as the carrier gas to demonstrate the possibility of the sensor to work under ambient conditions.

During the first 40 minutes, the carrier gas is laboratory air at a relative humidity of 7% (this low humidity value is chosen to show the large working range of the proposed sensor concept). After the installation of the bubbler (filled with distilled water) and an equilibration phase (cf., Experimental section), the carrier gas is humidified to a relative humidity of 55% (from 105 to 140 minutes). Upon this change of humidity, the electrical resistance of the sensor with a layer of PH 500 increases from 98 kΩ to 314 kΩ, while the electrical resistance of a sensor with a layer of the P VP AI 4083 decreases from 93 MΩ to 3 MΩ. Still, both sensors at both levels of humidity show an increase in electrical resistance upon exposure to ammonia, which is mixed to the carrier gas to achieve a concentration of 1% (exposure times to ammonia are 5 minutes).

The origin of the different electrical resistance changes for the two materials PH 500 and P VP AI 4083 upon contact to humidity is not yet fully understood. In general, water vapour affects PEDOT/PSS work functions,[15] leads to a change in film morphologies[17] (e.g. due to swelling) [23], can contribute to ionic conductivity,[16] can affect especially the DC conductivity by polarization effects, and also modifies the acid base chemistry of the materials (PSS acts as an acid in doping PEDOT). As we here report only the stable, time-independent components of the conductivity changes the latter effect resulting in changes in the doping level, possibly in conjunction with water-induced swelling of the layers appears most likely. Considering the different PEDOT to PSS ratios and especially the different film structures of the two materials (PH 500 is a homogenized version with small particle size), these effects can impact the sample resistivities in different ways.

It can also be seen from Fig. 4 that the first exposure of the devices to ammonia leads to a larger increase of the electrical resistance than subsequent exposures. Upon repeated exposures to a concentration of ammonia of 1% the device shows good reproducibility. Only upon the first few exposures an irreversible change of resistivity is observed.

The different response of the two sensor elements to a change of the ammonia concentration (resistivity increase in both samples) and to a change of the relative humidity (resistivity increase for PH 500 and decrease for P VP AI 4083 for an increase in humidity) allows the simultaneous determination of the ammonia and water concentration $C_{NH3}=f(R_1,R_2)$ and $C_{H2O}=g(R_1,R_2)$. The coefficients for using the power series method for f and g can be determined by a non-linear regression analysis to a series of measurements at varying (but known) ammonia and water concentrations.

4. Conclusion

In conclusion, a novel concept for a differential detection of ammonia in humid environements was realized, using two differently conducting formulations of commercially available PEDOT/PSS. Both materials show good sensitivity towards ammonia gas, which increases their electrical resistance by compensating the acid doping thus changing the hole density. In contrast, the two materials show an opposite change of their electrical resistance when they are exposed to varying humidity levels. This permits to separately determine both stimuli after a suitable calibration. The used materials are compatible with a number of printing techniques. Therefore, easy and cheap to produce sensor elements can be realized, which work under varying levels of humidity for the detection of ammonia in the sub-ppm region.

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Figure Captions:

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 AI 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).

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, in a gas flow of pure Ar.

Fig. 3 (color online) Electrical resistance of a sensor element with a drop-casted active layer of (a) Baytron PH 500 and (b) Baytron P VP AI 4083. The carrier gas is humidified argon (12.5% relative humidity). Shown are two succeeding exposures to 0.7 ppm ammonia.

Fig. 4 (color online) Electrical resistance of a sensor element with a drop-casted active layer of (a) Baytron PH 500 and (b) Baytron P VP AI 4083. The gas surrounding is dry- and humidified laboratory air (7% and 55% relative humidity - RH, respectively). Shown are two succeeding exposures of 5 minutes to 1% ammonia for each sensor element and for each humidity level. To increase visibility the values at 55% RH in (b) were multiplied by a factor of 20 (dotted line).

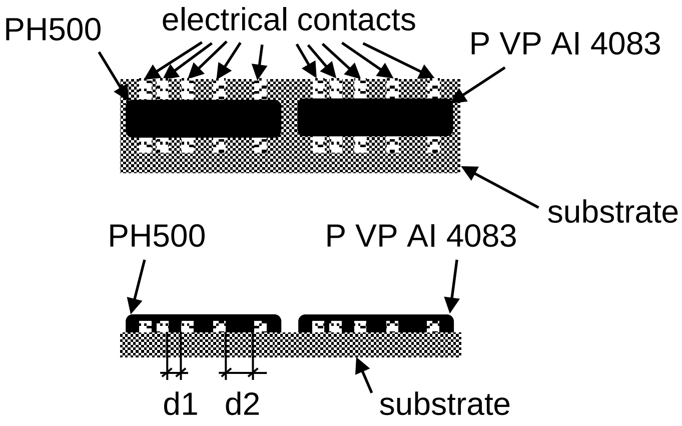
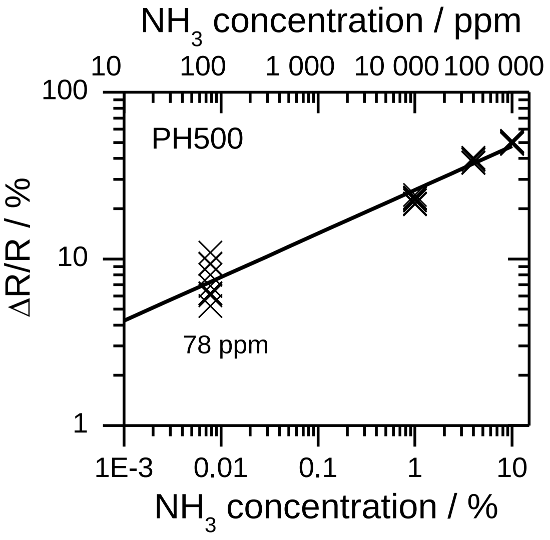

PH500
electrical contacts
P VP AI 4083
substrate
PH500
P VP AI 4083
d1
d2
substrate

Fig. 1



NH$_3$ concentration / ppm
10
100
1 000
10 000
100 000
100
10
1
ΔR/R / %
PH500
78 ppm
1E-3
0.01
0.1
1
10
NH$_3$ concentration / %

Fig. 2

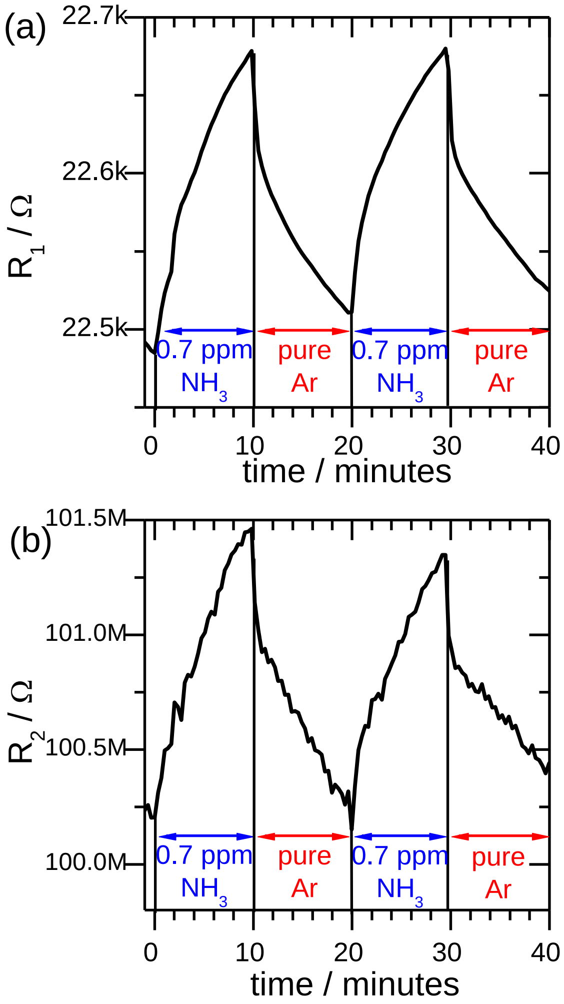

(a)
22.7k
22.6k
22.5k
R$_1$ / Ω
0.7 ppm NH$_3$
pure Ar
0.7 ppm NH$_3$
pure Ar
0
10
20
30
40
time / minutes
(b)
101.5M
101.0M
100.5M
100.0M
R$_2$ / Ω
0.7 ppm NH$_3$
pure Ar
0.7 ppm NH$_3$
pure Ar
0
10
20
30
40
time / minutes

Fig.3

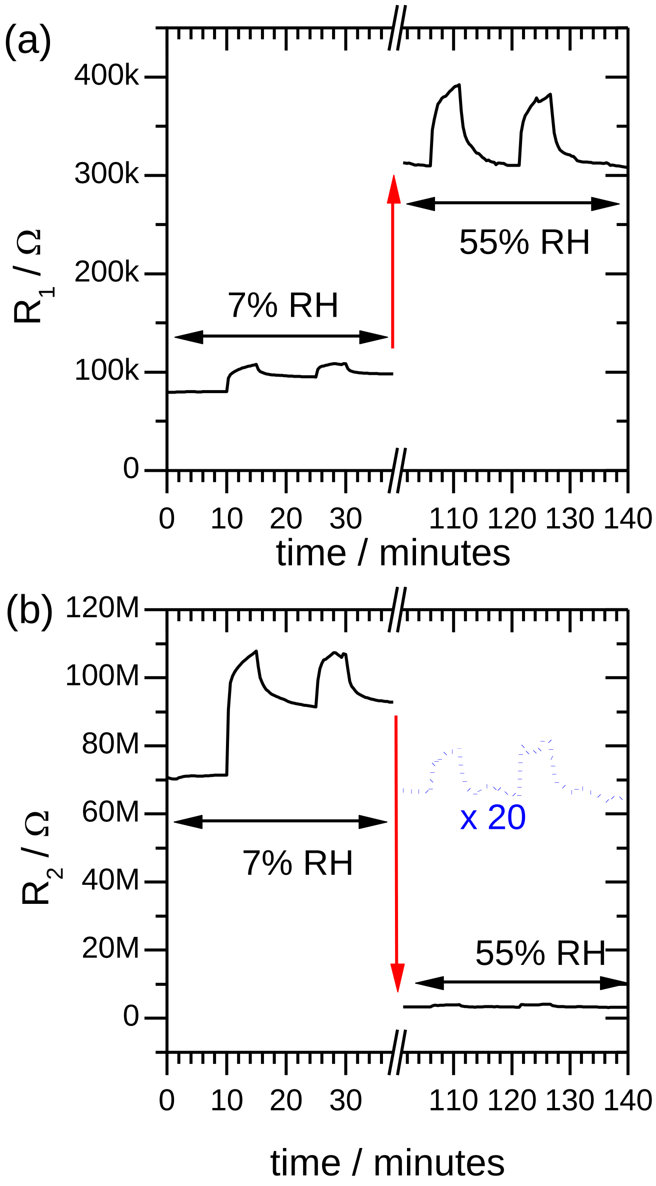

(a)
400k
300k
200k
100k
0
R_1 / Ω
7% RH
55% RH
0
10
20
30
110
120
130
140
time / minutes
(b)
120M
100M
80M
60M
40M
20M
0
R_2 / Ω
7% RH
x 20
55% RH
0
10
20
30
110
120
130
140
time / minutes

Fig.4

Author biographies

Peter Pacher studied technical physics at the Graz University of Technology in Austria, where he obtained his master degree in 2003. He completed his Ph.D in 2008 working on organic thin film transistors and organic resistors for sensor applications and worked as a PostDoc in the group of Prof. Zojer in the field of organic sensors. Today, Dr. Pacher works in a private enterprise in the field of patents.

Alexandra Lex received her PhD in chemistry from the University of Technology Graz in 2008. She is currently working at the Westfälische Wilhelms-University Münster in the field of lithium-ion-batteries.

Sabrina Eder obtained her diploma (masters degree) at the Graz University of Technology in 2007 and is currently employed as a PhD student at the University of Bergen in Norway. Her current field of research is neutral atom microscopy.

Gregor Trimmel received his PhD from the Vienna University of Technology, Austria, in 2000. He presently is an Universitätsdozent for Macromolecular Chemistry in the Institute for Chemistry and Technology of Materials at the Graz University of Technology, Austria, and Director of the Christian Doppler Pilotlaboratory for Nanocomposite Solar Cells. His research interest are focussed on nanocomposite solar cells, surface functionalization of organic thin films, and self assembly of block copolymers.

Christian Slugovc obtained his Diploma and his PhD from Vienna University of Technology in 1996 and 1998, respectively. He did post-doctoral research with Ernesto Carmona at the

CSIC in Sevilla. In 2002 he moved to Graz University of Technology (TU Graz) and finished his Habilitation in 2007. Currently he is associate professor (Universitätsdozent) at the Institute of Chemistry and Technology of Materials (ICTM) of TU Graz and is vice head of this institute. His research interests comprise olefin metathesis (organometallic and macromolecular aspects), electroactive materials and sensor materials.

Emil J.W List received his PhD in 2000 from the Graz University of Technology and was appointed Associate Professor (Habilitation in Solid State Physics) in 2003. In addition to his academic activities at TU Graz, since 2007 he holds the position of the Scientific Managing Director of the newly founded NTC Weiz GmbH. Emil J. W. List is an expert in the field of organic semiconductor devices and optical spectroscopy of conjugated polymers.

Egbert Zojer received his diploma and PhD in 1996 and 1999 from the Graz University of Technology, where he currently holds an Associate Professor position. He spent several years in the US at the University of Arizona and the Georgia Institute of Technology, where he worked with Jean-Luc Brédas. His current research interests include organic thin film transistors and sensors as well as the quantum-mechanical modeling of organic semiconductors.