Effect of Humidity on Ammonia Gas Sensitivity of Intrinsically Conducting Composite Films

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Summary: The effect of humidity on the ammonia gas (NH_3) detection of conducting composite films was investigated. The first results showed that the presence of humidity, acting as interference gas, modifies the behaviour of sensors in the presence of ammonia. However, the behaviour study at atmosphere without ammonia of our materials in controlled temperature and humidity allowed distinguishing atmospheric effect from NH_3 pollution.

Keywords: ammonia; humidity; polyaniline; sensor

Introduction

Among all intrinsically conducting polymers (ICPs), polyaniline (PANI) has achieved widespread importance thanks to its unique conduction mechanism and high environmental stability. Chemical sensors based on ICP as sensing material have been recently studied. Conducting polymers offer major advantages towards oxide sensors or other organic materials as porphyrins, phtalocyanins. Indeed, ICP sensors are easy to process. They may also have reversible response along with high sensitivity and short response time. However, all these performances still depend on the sensor tailoring, the ICP composition, the film deposit and the chemical species to be detected. PANI was found to be the best choice to detect gases such as ammonia.

Our work is based on a PANI/polymer matrice composite easy to synthesize and to process with respect to environmental and human safety requirements. The sensing film is formed after the water evaporation by adjusting the composite formulation. This low cost, environmental friendly and easy process favours any future industrial transfer.

Our first work revealed that the NH_3 sensor using PANI/polymer matrice composite could potentially provide the following advantages: good mechanical stability, ease of measurement, reversibility and good sensitivity.

Other shortcomings of gas sensors using conducting polymers include selectivity of the response towards a specific gas in various coexisting gases. All gases that are high oxidizing or reducing as well as high basic or acidic agents potentially affect the PANI electrical conductivity. It is well known that interaction with water vapour also affect conductivity of PANI. Consequently, humidity is a parameter that must be dealt within the development of a reliable NH_3 sensor device.

In this study, the effects of humidity and temperature on the sensor response to NH_3 were studied and the results have been compared to the behaviour obtained in atmosphere free of NH_3.

Experimental Part

Conducting Composite

Core-Shell Polybutylacrylate-Polyaniline Latex Particles

Composite latex particles were synthesized according to the procedure developed by

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Kohut-Svelko *et al.*[4,7]. In a typical polymerization, reaction mixture of non ionic surfactants (NP40 and Ninol, 3.40 g) was dissolved in distilled water (200 mL) in a three-necked round-bottom flask under a nitrogen atmosphere. The purified monomer butylacrylate (87 g, 0.679 mol) was added to the aqueous solution and emulsified under vigorous stirring. This emulsion was then heated under mechanical stirring up to 70 °C. The aqueous solution of ammonium persulfate (0.3 g in 5 mL of water) was then added drop by drop. The polymerization was allowed to proceed for 24 h at 70 °C under mechanical stirring. In a second stage, anilinium salt is used as monomer and added to the above emulsion to create a core-shell structure. The concentration of anilinium salt was kept constant (15 mg/mL) and the solid content of the PBuA latex is adjusted with the respect to the expected core-shell ratio. Neither additional acid, nor surfactant was added to the reaction mixture. The core dispersion containing the anilinium salt was let under stirring for 20 min before to be cooled down to 0 °C for one hour. The initiator (ammonium persulfate in water) was then added drop by drop to the above dispersion ([oxidant]/[anilinium salt] = 1). Polymerization was carried out under nitrogen and mechanical stirring; the temperature was maintained at 0 °C for 5 hours.

Gas Sensor

The PANI composite as core-shell particles is obtained in aqueous dispersion in soft experimental conditions with no external acid, organic solvent or post treatment as previously described. For the sensor active layer deposit, the dispersed medium is first let under sonification for 5 to 10 min before to be spread with an airbrush onto a substrate. After evaporation of solvent (water), a thin film was formed (from 30 to 50 μm) and it may be incorporated into a sensor system. The resistance of conducting polymers is measured by a 4 probes method connected to a multimeter Keithley 2000. The sensors were exposed in a dynamic exposure chamber where the ammonia concentration, temperature, relative humidity are controlled. The experimental system is detailed in Figure 1.

Results and Discussion

Core-shell Conducting Particles in Gas Sensors

The principle of the ammonia sensor containing PANI as sensing material is described in Figure 2.

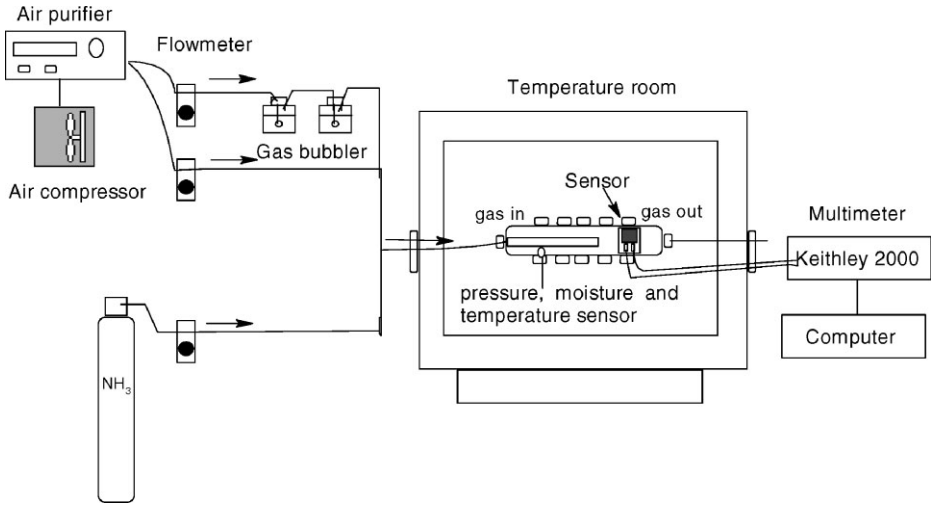

Figure 1.
Scheme of the exposure chamber system used to test the ammonia sensor.

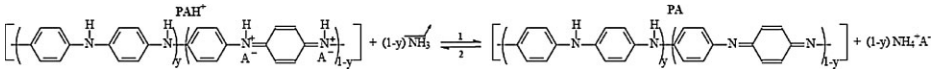

Figure 2.
Redox reaction of PANI under ammonia exposure (1) and fresh air (2) with PAH^+ as emeraldine salt (PANI conducting form) and PA emeraldine base (PANI insulator form).

When the sensor is exposed, ammonia takes up protons from PANI, to form energetically more favourable ammonium species, NH_4^+. This is the PANI dedoping reaction and the resistance of the composite increases. As soon as the composite is in atmosphere free of ammonia, the reaction is shifted towards the left. Ammonium decomposes into ammonia and protons, being added to PANI, restore the initial level of doping[8].

Influence of Humidity without Ammonia Pollution

The work concerning the influence of humidity onto the gas sensor was studied. Our first results showed that the variation of resistance could be modelled between 10 and 30 °C and from 20 to 90% of relative humidity (r.h.) in a standard atmosphere (Figure 3). *Ref* is the resistance at 25 °C and 50% of relative humidity, thus *R/Ref* is a ratio of the experimental resistance versus resistance at 25 °C and 50% r.h. *T* and *H* are respectively temperature in Celsius degrees and relative humidity in %.

It is worth noticing that the variation of sensitivity (*R/Ref*) essentially depends on humidity and a parameter coupling temperature and humidity. The influence of temperature alone is negligible. However, under any experimental condition, the devices exhibit the lowest conductivity and so the lowest sensitivity when humidity parameter is close to the 50%. Below and above 50% r.h, the conductivity increases but not in the same manner i.e. the sensitivity at 10 °C is lower at 20% r.h. that at 80% r.h. and the latter is also higher than at 30 °C. This phenomenon can be explained considering that the active layer made of conducting composites is synthesized in waterborne system. So, this active layer needs to be subjected to a certain humidity content (50% r.h to reach its maximum of conductivity). However, once this level reached, the surplus of water causes a reduction of conductivity. This behaviour was previously reported by others[9]. This phenomenon could be explained by the fact than the conductivity enhancement is due to an increased size of the conducting islands in the presence of humidity[10].

Influence of Humidity in the Presence of Ammonia Pollution

It is interesting to compare the above results (Figure 3) with the sensor behaviour

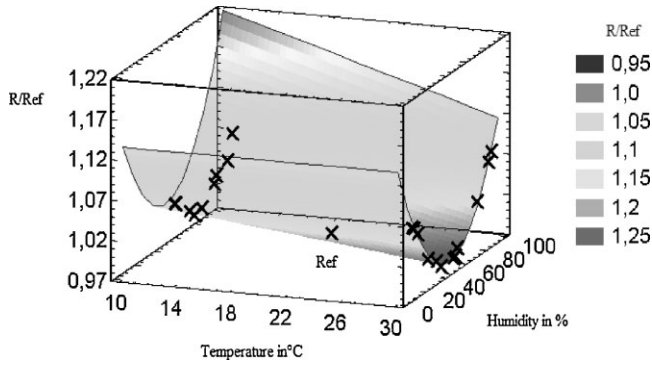

Figure 3.
Behaviour of resistance between 10 and 30 °C between 20 and 90% of humidity in neutral atmosphere.

in the presence of ammonia in various conditions of temperature and humidity (Figure 4). In this Figure, R/R_0 is the ratio of the experimental resistance versus the initial value as measured before ammonia exposure in the same conditions.

In Figure 4b, the results showed that sensors in the presence of 50 ppm ammonia exhibit the lowest sensitivity (R/R_0) when the relative humidity is close to 50%, as previously described under air free of ammonia. Moreover, under ammonia

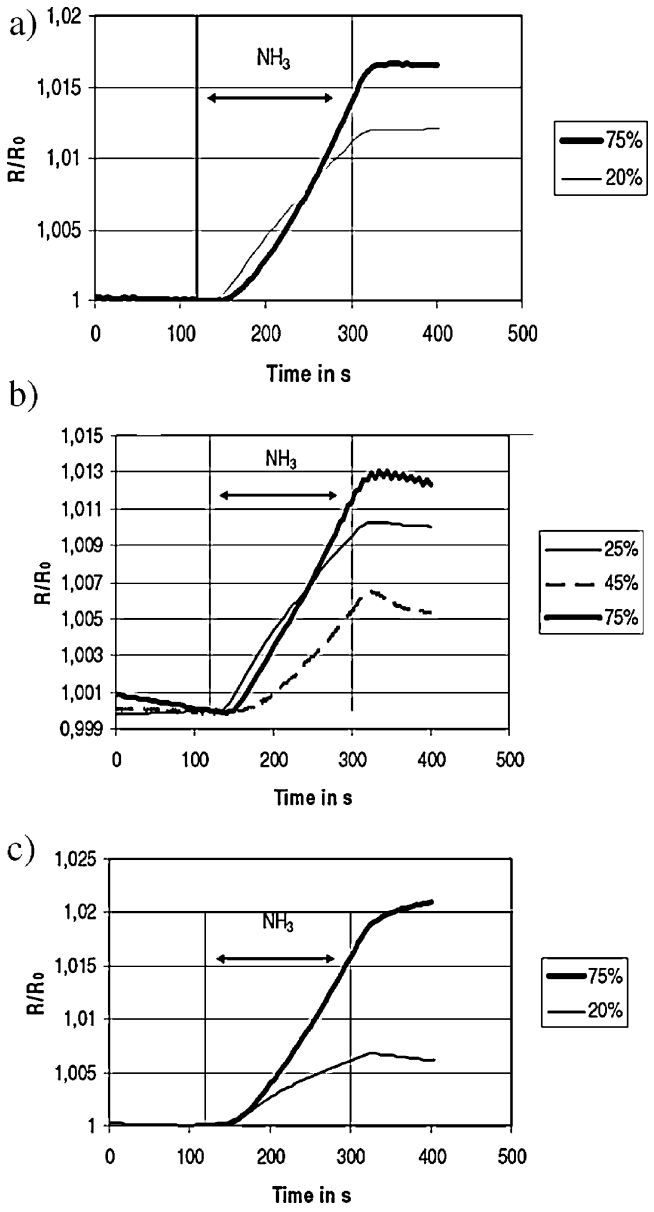

Figure 4.
Sensor behaviour when exposed in 50 ppm ammonia for 3 min in various humidity (a) at 10 °C (b) at 25 °C (c) at 30 °C.

pollution, the overall dependence of sensor sensitivity upon humidity and temperature is the same as previously observed (Figure 3). Indeed, the sensitivity gap at 30 °C when the relative humidity increases from 20 to 75% is higher that those observed at 10 °C (Figures 4a and 4c). This behaviour is not due to the ammonia in the air but to the atmospheric conditions and it is possible to distinguish both effects. Therefore, it is possible to predict the behaviour of our new ammonia sensor in various conditions.

Conclusion

Film composites containing an intrinsically conducting polymer (ICP), i.e. polyaniline have been successfully employed in chemical sensor device. The strategy offers many advantages: the film composite is performed by a easy, low cost and environmentally friendly process. Moreover, the devices already showed good sensitivity and reversibility under ammonia exposure. This paper reports that the sensor behaviour could be predicted under specific atmospheric conditions as temperature and humidity parameters. Future works will include modelling of the behaviour in various ammonia pollution (concentration, time of exposure...). In the same time, we still work to improve sensitivity and selectivity of the sensor.

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