Sensing of NH₃ on heterogeneous nanoporous carbons in the presence of humidity

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Abstract

The influence of humidity on the NH_3 detection capability of S- and N-containing nanoporous carbons was examined for the first time. To investigate the role of water on the electrical performance of the sensors, the sensing tests were carried out using a flow of NH_3 diluted in moist air. The same tests were also carried out by performing a 2 hours prehumidification prior to the exposure of the carbons to the moist gas stream. Compared to dry conditions, the presence of water in the air stream led to an enhanced response of the sensor. On the other hand, upon the prehumidification the adsorbent's surface an opposite outcome was recorded. Based on the electrical behavior of the carbons and their extensive surface characterization, a complex sensing mechanism is proposed. This mechanism includes specific interactions of NH_3 and H_2O molecules with surface functionalities, such as hydrogen bonding, proton transport through ionic conductivity, and electron-hole conductivity.

KEYWORDS: *ammonia gas sensors, nanoporous carbons, surface chemistry, humidity, ammonia adsorption, surface heterogeneity.*

1. Introduction

Ammonia (NH_3) is a colorless gas with pungent odor and high toxicity. Its main natural source is from agricultural industries and metabolic processes [1-3]. The permissible exposure limit for ammonia according to OSHA is 50 ppm over an 8-h work day or a 40-h work week, while exposure to 300 - 500 ppm has been reported as the maximum short exposure tolerance [4,5]. Therefore, its detection at low concentrations is crucial in various fields including chemical industries, medical diagnosis, or fertilizer factories. When ammonia is dissolved in water,

aqueous ammonia is formed. It is a colorless solution that may severely irritate the respiratory tract. Moreover, the exposure to aqueous ammonia can lead to skin and eye burns [6].

Carbon-based materials, such as graphene oxide, mechanically exfoliated graphene sheets or carbon nanotubes (CNTs) have been extensively used as ammonia gas sensors. They behave as p-type semiconductors, with holes (h^+) being the main charge carriers. Upon their exposure to electron donating gasses, such as ammonia, an increase in their normalized resistance is usually observed as a result of the reduction of holes [7-16]. These materials, even though sensitive towards the target gas, lack the selectivity. Therefore, a surface functionalization, including a metal-doping or polymer-coating are usually applied. In our recent studies we have tested the ammonia sensing capability of nanoporous carbons [17,18]. Because of their rich surface chemistry and developed porosity, these materials showed good sensitivity and selectivity towards NH_3 , without the need of any of the above-mentioned treatments.

Since air moisture may be adsorbed on the surface of the carbon-based materials and react with the target gas, humidity is a crucial parameter that has to be considered upon the fabrication of a reliable ammonia sensor. Graphene-based materials have been previously studied as humidity sensors [19-24]. It was shown that at low relative humidity (RH), these p-type materials exhibit an increase in the resistance owing to the hole depletion that is caused by electrons donated by the adsorbed water molecules [19,25]. At even higher relative humidity (RH), multilayers of physically adsorbed water molecules condense mainly in the capillary pores and hydronium (H_3O^+) ions are formed. Here a charge transfer occurs through the well-known Grotthuss's chain reaction, which eventually leads to a decrease in a sensor's resistance [19,26].

In the case of activated carbons, the adsorption behavior of water is different than that of simple fluids and it is based mainly on the formation of hydrogen bonds between the water

molecules and surface functional groups [27,28]. It has been reported that the presence of water in the pore structure of nanoporous carbons enhances the adsorption of some gasses, such as ammonia [29,32] or hydrogen sulfide [33-35]. In the case of NH_3 , that enhancement is related to the dissolution of the gas in the water film that is formed in the carbon micropores. Nevertheless, in some cases it has been found that water instead of enhancing NH_3 uptake, actually diminishes it, which is linked to the competition between ammonia and water for adsorption centers [30].

The objective of this study is to explore the ammonia sensing capability of S- and N-containing nanoporous carbons [36] under moist conditions. This kind of investigation is important in order to test a performance of sensors in real-life conditions. For this purpose, moist gas stream is used and the chips are either dry or with water preadsorbed on the surface of our activated carbon (two hours prehumidification). These carbons have been previously tested as ammonia sensors in dry conditions, and it was found that their surface heterogeneity played a key-role governing their electrical behavior [37]. The chips made of two carbon samples are referred to as C-AO and C-BO. The sensing materials were obtained by air oxidation of two polymer-derived carbons (C-A and C-B, respectively) addressed in details in the experimental section and Ref. [36].

2. Experimental

2.1 Preparation of materials

Two carbon samples were studied, which are referred to as C-AO and C-BO. They were obtained after a 3 hours air oxidation, of two independent series of polymer-based carbons (C-A and C-B), at 350 °C. The polymer precursors used for the preparation of C-A and C-B, were poly

(4-ammonium styrene-sulfonic acid) and a 1:1 mixture of 30% solution of poly (4-ammonium styrene-sulfonic acid) and Poly(4-styrenesulfonic acid-co-maleic acid) sodium salt, respectively. These polymer sets were carbonized at 800 °C for 40 min with a heating rate of 50 °C/min. The flow of N₂ was 300 mL/min.

2.2 Preparation of sensor chips

The gas sensor chips were prepared by coating (using a blade) 8 mm × 8 mm thin-film gold interdigitated electrodes, with 50 µm lines/spaces on alumina substrate, with a slurry made of the tested carbons. The coated chips were dried at 120 °C for 24 hours. The thickness of the obtained film was ~15 µm.

2.3 Sensing procedure

For the sensing test, each chip after being coated with the active materials and dried, was placed in a 20 cm³ home-made gas chamber, which was purged with dry air to establish a dynamic equilibrium. A VersaSTAT MC (AMETEK, Princeton Applied Research) was employed for monitoring the electrical measurements and sensing performance, through four-wires, at room temperature, and applying 1 V voltage. The reversible sensing was performed by exposing the chips to six different ammonia concentrations (45-500 ppm), with a total flow rate of 500 mL/min. From the data obtained, the normalized change in resistance ($\Delta R / R_o = (R_t - R_o) / R_o$) was calculated, where R_o is the resistance of the sensor before exposure to NH₃, and R_t is the resistance at any time, t . The experimental set-up is illustrated in Figure 1.

Figure 1. The experimental set-up.

2.4. Surface characterization

2.4.1. NH_3 breakthrough dynamic test: For the determination of an ammonia breakthrough capacity, dynamic breakthrough tests were performed at ambient conditions. Even though the equilibrium is not reached, analyzing the existed samples provides the needed information about changes in the surface chemistry caused by ammonia exposure. Unfortunately, the active material from the chips cannot be used for this purpose owing to its very small quantity. In a typical run, a stream of ammonia diluted with air passed through a glass column (length 370 mm, internal diameter 9 mm) packed with the adsorbents. The bed volume used was $\sim 2 \text{ cm}^3$ (particle size 1 - 2 mm), while the total inlet flow rate was 225 mL min^{-1} with an ammonia concentration of 1000 ppm. Ammonia breakthrough was monitored using an electrochemical sensor (Multi-Gas Monitor ITX system) and its flow was arbitrarily stopped at the breakthrough concentration of 100 ppm (a sensor limit). Tests in moist conditions were implemented by diluting the

ammonia stream with a moist air stream (70% humidity). The same tests were also performed after a 2 hours prehumification of the samples. The suffixes –EM and -EPM are added to the name of the resulting exhausted samples, respectively.

2.4.2. Potentiometric titration: Potentiometric titration measurements were performed using a Titrand 888 automatic titrator (Metrohm). The procedure is described in details elsewhere [38]. For the evaluation of the surface properties, it was assumed that the population of sites can be described by a continuous pK_a distribution, $f(pK_a)$. The experimental data were transformed into proton binding curves, Q , representing the total amount of protonated sites. From them the pK_a distributions and the numbers of groups represented by certain pK_a values were calculated [39,40].

2.4.3. Sorption of nitrogen: Sorption of nitrogen was carried out using ASAP 2020 (Micromeritics). The samples were outgassed at 120 °C to constant vacuum (10^{-4} kPa), prior the experiments. 120 °C was chosen as the outgassing temperature to remove the physically adsorbed species without altering the surface chemistry. The surface areas (BET method), total pore volumes (V_t) (from the last point of isotherm at a relative pressure equal to 0.99), volume of micropores (V_{mic}), volume of pores smaller than 1 nm ($V_{<1nm}$), volume of pores smaller than 0.7 nm ($V_{<0.7nm}$), volume of mesopores (V_{mes}), and pore size distributions were calculated from the isotherms obtained. For the calculation of the pore size distributions, the Non-Local Density Functional Theory (NLDFT) was used (free download at www.nldft.com) [41,42].

2.4.4. XPS: X-ray photoelectron spectroscopy (XPS) analysis was used to determine the surface chemistry of the carbons studied. A Physical Electronics spectrometer (PHI 5700), equipped with $MgK\alpha$ X-ray radiation (1253.6 eV) as the excitation source was used, at a base pressure of 5×10^{-9} Torr. Prior to XPS analysis the samples were outgassed overnight at 10^{-8} Torr, at room

temperature. After this vacuuming process, only the weakly adsorbed species get desorbed. High resolution spectra were recorded at a take-off angle of 45° by using a concentric hemispherical analyzer operating in constant-pass-energy mode at 29.35 eV, with a 720 μm diameter analysis area.

2.4.5. Affinity to adsorb water: The affinity of carbons to adsorb water was evaluated by exposing predetermined amounts of dry carbon samples for 24 h either to water vapors, in air-tight environment and at room temperature. The adsorbed amount (in wt. %) was determined from the weight difference of the carbons before and after the exposure.

3. Results and Discussion

3.1. Sensing response and surface characterization

Figure 2 shows the changes in a normalized resistance upon the initial exposure of C-AO and C-BO to 500 ppm of NH_3 followed by a subsequent air purging. In order to determine the role of water, the samples were either directly exposed to a humid gas stream (Figure 2A) or they did undergo a two hours prehumidification prior their exposure to the target gas (Figures 2B and 2C). In the former case, both samples exhibited a decrease in their normalized resistance. This decrease was almost three times greater for C-AO than that for C-BO (50% and 17.7%, respectively). After the signal reached a steady state, which is related to the exhaustion of the active adsorption sites of the carbons' surface, the chamber was purged with moist air in order to determine the extent of chemical/physical NH_3 adsorption. A very small resistance increase for both carbons, (1.5% for C-AO and 1.3 % for C-BO) indicates that in the presence of moisture chemisorption affects more the surface of the carbon compared to the same process in dry conditions [37]. At the latter ones the corresponding values of a resistance increase were 6.7% for C-AO and 4.4% for C-BO [37].

Figures 2B and 2C present the initial stabilization of the signals in ammonia in moist air, after a two hours prehumidification of the chips. Upon exposure to ammonia, the normalized resistance of C-AO increases about 225% and it takes about five hours for the signal to stabilize. For C-BO on the other hand, even though its resistance increases 160%, the signal does not reach the plateau even after a 24 h exposure to NH_3 .

Figure 2. Normalized change in a resistance for C-AO and C-BO upon their initial exposure to a humid gas stream (A) and a humid gas stream with two hours prehumidification (B and C).

To examine the reversible sensing capability of our carbons in moist conditions, after the initial stabilization step the chips were exposed to ammonia concentrations varying from 45-500 ppm. Figure 3A illustrates the sensing curves of C-AO and C-BO upon their immediate exposure to NH_3 /moist air cycles (without prehumidification). Even though both carbons show similar trends in their electrical behavior, C-AO exhibits twice larger signal change compared to that for C-BO. Interestingly, while for C-AO a direct exposure to a humid gas stream led to a considerable increase in the normalized resistance compared to dry conditions ($\sim 34.9\%$ at moist vs. 14.1% at dry [37], for 500 ppm of NH_3 , Table 1), for C-BO, on the other hand, moisture in the challenge gas didn't cause any changes in the extent of its electrical signal ($\sim 6.3\%$ at moist vs. 6.2% at dry [37], for 500 ppm of NH_3 , Table 1). After the 2-hours prehumidification (Figures

3B and 3C), smaller signal changes were observed for both carbons (~6.3% for C-AO and ~5.1% for C-BO, Table 1) in comparison to those when the samples were directly exposed to the moist gas stream. Furthermore, for both carbon samples, the normalized resistance changes linearly with increasing ammonia concentrations, as indicated in Figures 3D and 3E. In these Figures the reproducibility of the sensing results is illustrated too. The collected data is based on measurements on three different chips for each sample, with error bars indicating the standard deviation. The relative σ (% RSD) was found to be between 4.6-7.5 % for the C-AO series, and 3.9-9.7% for the C-BO series.

Figure 3. Response curves for C-AO and C-BO upon exposure to NH₃/moist air cycles (A) without prehumidification and (B, C) after prehumidification. For each concentration two sensing cycles are given. Dependence of the normalized resistance change on the various ammonia concentrations for the samples with (D) and without (E) prehumidification.

Table 1. Change of normalized resistance $\Delta R/R_o$ [%] of the C-AO and C-BO carbon chips upon exposure to various ammonia concentrations in the moist conditions.

% change of normalized resistance [$\Delta R / R_o$]				
Concentration [ppm]	C-AO-EM	C-BO-EM	C-AO-EPM	C-BO-EPM
500	34.85	6.27	6.33	5.13
375	26.60	4.77	5.15	4.13
250	23.07	4.17	4.53	3.30
175	17.02	3.00	3.26	2.60
100	12.14	2.24	2.40	1.89
45	9.52	1.78	2.00	1.28

To understand the factors that govern the electrical behavior of our carbons and to derive a sensing mechanism, NH₃ breakthrough tests were carried out and the exhausted samples were extensively characterized. The samples were either exposed directly to a wet NH₃ stream (70% humidity) or they were exposed to moist air for 2 hours, prior to their exposure to the wet ammonia stream. The suffixes –EM and -EPM are added to the names of the resulting exhausted carbon samples. The measured breakthrough curves on our carbons along with the desorption curves and NH₃ breakthrough capacity values are presented in Figure 4. The tests were arbitrary stopped at 100 ppm (a sensor limit).

Figure 4. Ammonia breakthrough and desorption curves. Data for C-AO-ED and C-BO-ED taken from Reference [37]. Copyright 2015, with permission from Elsevier.

While in the case of the C-AO carbon, water did not improve ammonia retention, when being present in the target gas, upon its preadsorption on the adsorbent's surface, a slight improvement was observed. In the former case, the negative effect of water on the NH_3 uptake is likely related to the competition between both molecules for the same adsorption sites. For the C-BO carbon on the other hand, water plays an enhancing role in the retention of the target gas, which is related to the effect of H_2O on this sample's acidity. More precisely, water favors the deprotonation of carboxylic groups [29], which can then chemically react with ammonium ions. Upon prehumidification of the adsorbents, gaps between the adsorption and desorption curves are revealed, which indicates weak interactions of the target gas with the activated carbons. This gap is observed due to a marked desorption and the lack of data above 100 ppm of ammonia (sensor's limit).

The results obtained from potentiometric titration experiments are presented in Figure 5. For all exhausted samples, a peak at pK_a 9–10 is assigned to NH_4^+ formed as a result of ammonia dissolution in water and/or acid-base reactions of NH_3 with acidic functional groups. It is worth

mentioning that for C-AO-EPM the intensity of this peak is significantly smaller compared to that for C-AO-EM. For the C-BO exhausted carbon series, this peak has the highest intensity for C-BO-EM. In the case of C-AO-EPM an additional peak at pK_a 10-11 is revealed. It might represent nitro-type complexes [43]. In order to account for the differences in the species detected on the surfaces of the two sample series, we further analyzed the nature of the surface functionalities as well as the potential interactions between ammonia, water and the carbons' surface.

Figure 5. The pK_a distributions of the species present on the surfaces of the initial and exhausted carbons.

The parameters of the porous structure for the initial and exhausted samples are presented in Table 2. The results show that for both exhausted carbon series, the changes in the pore volume follow opposite trends, whether moisture is present in the challenging gas or it is preadsorbed on the carbons' surface. More precisely, the C-AO exhausted carbon series exhibit a decrease in the volume of both mesopores and micropores, which is likely related to the presence of deposited products of surface reactions at the pore entrances. On the other hand, for the C-BO exhausted samples the volume of mesopores increases with almost negligible changes in the volume of ultramicropores. The observed increase could be related to the removal of bulky

functionalities and/or carbon atoms from the walls of micropores. To be able to further interpret the changes in the porosity of the exhausted samples, the affinity of each carbon to adsorb water and their surface chemistry were analyzed.

Table 2. Parameters of the porous structure calculated from the nitrogen adsorption isotherms.

Sample	S_{BET} [m ² /g]	S_{NLDFT} [m ² /g]	V_t [cm ³ /g]	V_{meso} [cm ³ /g]	V_{mic} [cm ³ /g]	$V_{<0.7\text{nm}}$ [cm ³ /g]	$V_{<1\text{nm}}$ [cm ³ /g]	V_{mic}/V_t
^a C-AO	11	995	0.363	0.024	0.339	0.215	0.281	0.93
^b C-AO-ED	554	761	0.301	0.054	0.247	0.182	0.203	0.82
C-AO-EM	543	792	0.272	0.014	0.258	0.191	0.218	0.95
C-AO-EPM	496	728	0.247	0.011	0.236	0.176	0.204	0.83
^a C-BO	847	1183	0.458	0.060	0.398	0.266	0.339	0.87
^b C-BO-ED	823	1143	0.453	0.075	0.378	0.273	0.320	0.83
C-BO-EM	852	1189	0.486	0.097	0.389	0.271	0.332	0.80
C-BO-EPM	859	1200	0.492	0.100	0.392	0.275	0.335	0.80

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^bdata taken from Reference [37]. Copyright 2015, with permission from Elsevier.

The results of the XPS analyses including the content of elements on the surface in atomic % and the deconvolution results of core energy level spectra are summarized in Figure 6. Figure 6A shows that C-BO-EM exhibits the most significant changes in the total content of O, N and S, compared to the rest of the samples. A fourfold increase in the total content of nitrogen, and an almost threefold decrease in the total content of oxygen were found. A possible explanation for this is the high reactivity of this sample with ammonia and thus incorporation of more nitrogen to the surface of this carbon, as a result of ammonia reaction with surface oxygen functionalities.

Figure. 6 A) Content of elements; B-E) Surface concentration of the specific carbon, oxygen, nitrogen and sulfur groups. Due to the complexity of the species, the components of the N 1s core energy level spectra are referred to as N-1 (pyridines), N-2

(pyrroles/ammonia/amines/amides), N-3 (quaternary nitrogen and/or protonated amines) and N-4 (NH_4^+ and/or NO_x species). Data for the initial carbons is taken from Ref. [36]. Copyright 2014, with permission from Elsevier.

Based on the deconvolution of S 2*p* core level spectra, for C-AO-EM, C-BO-EM and C-BO-EPM, an increase in the contribution of reduced sulfur species is observed and a decrease in the relative concentration of sulfur in sulfones and sulfoxides. This is related to the electron donating character of both ammonia and water. C-AO-EPM, on the other hand, unlike the rest of the samples, exhibits negligible changes in the relative concentration of sulfur in the reduced forms. This finding, along with the increased contribution of superoxide ions based on the deconvolution of O 1*s*, suggests that the surface of C-AO-EPM underwent some degree of oxidation. The components of the N 1*s* core energy level spectrum at 398.7 eV, 400.1 eV, 401.3 eV and 402.5 eV are referred to as N-1, N-2, N-3 and N-4, respectively. In the N-1 category we include pyridines, in N-2-pyrroles/ammonia/amines/amides, in N-3-quaternary nitrogen and/or protonated amines and in N-4- NH_4^+ and/or NO_2 species. A closer look at the deconvolution of N 1*s*, shows that an increase in the contribution of pyridines (N-1), pyrroles and amines (N-2) was found. The former two have been previously reported to promote the formation of active oxygen species (O_2^-), due to the activation of the surface oxygen by electrons donated from the nitrogen atoms in these species [44,45]. According to previous studies, in the presence of chemisorbed oxygen species, ammonia may react with them forming NO and N_2O [46-49]. O_2^- may further transform the relatively unreactive NO to NO_2 , which is a strong oxidant. Based on this, in our case, the increased contribution of NO_x species for the exhausted samples is likely related to the oxidizing activity of superoxide ions towards NH_3 . The formation of nitro-type complexes was also suggested from the analysis of the potentiometric titration results discussed above.

From the deconvolution of N 1s, it is also seen that C-BO-EM exhibits the largest increase in the contribution of ammonium ions (N-4). This might explain the decrease in its micro- and ultramicropore volume. The acid-base reactions of ammonia with carboxylic and sulfonic groups are the main pathways for the formation of surface ammonium salts (NH_4^+ ion). These reactions are further verified by decreased contributions of carboxylic and sulfonic groups, based on the deconvolution of the C 1s and S 2p core level spectra. C-BO-EPM also exhibits changes in the contribution of acids, similar to those of C-BO-EM. However, due to the preadsorption of water on its surface, the formation of NH_4^+ is likely linked to the dissolution of NH_3 in water rather than to acid-base interactions. Unlike in the case of C-BO-EM, for C-BO-EPM an increased contribution of sulfonic acids is found.

Both exhausted carbon series (C-AO-EM, C-AO-EPM and C-BO-EM, C-BO-EPM) show differences in the contribution of amines and pyrrolic groups (N-2) compared to the initial samples, based on the deconvolution of the N 1s. While C-AO-EM and C-AO-EPM exhibit a slight decrease and increase, respectively, C-BO-EM and C-BO-EPM on the other hand, exhibit an about 27% increase. This indicates that the target gas interacts in different ways with the matrices of each carbon series. Considering that both carbons exhibit similar -S, -N and -O surface functionalities, to account for the trends found, the accessibility of water to the pore system of each carbon and therefore the extent of the amount of ammonia dissolved in water is a crucial quantity which is discussed below.

It is important to mention that to characterize the exhausted samples using XPS analysis and nitrogen adsorption, a high vacuum was applied, which most likely caused the removal of weakly retained NH_3 molecules that were not able to be removed at ambient conditions, during the ammonia desorption step. As mentioned earlier in this paper, prior to the reversible sensing,

an ammonia stabilization step occurs (Figure 2), during which reactive adsorption of ammonia takes place. It causes the exhaustion of the carbons' reactive sites. Since the reversible sensing is based on the weak interactions between NH_3 and the exhausted samples, the chemical nature of the latter is very important.

3.2. Sensing mechanism

Based on the electrical behavior of the carbons and their extensive surface characterization, a sensing mechanism is proposed. For both samples, when moisture is present in the carrier gas without a prior chip prehumidification (C-AO-EM and C-BO-EM), water and ammonia compete for the same adsorption sites. In that case, water molecules occupy some sites of the carbons that would otherwise be available for interactions with NH_3 . These sites consist of -O, -S and N-containing surface functionalities, such as sulfoxides, sulfones, thiols, phenols, alcohols, carboxylic groups, positively charged pyridine-N-oxides, and negatively charged pyridines. In addition to the evidence given by the ammonia breakthrough test, the competition between these two species is also visible in the electrical behavior of the carbon chips at a typical NH_3 /moist-air sensing cycle (Figure 7A). As seen in Figure 7A, upon exposure of the chips to NH_3 , a small decrease in the normalized resistance is observed (I_A) which is followed by a larger increase in this value (II_A). On the other hand, upon purging the chamber with moist air, an exactly opposite trend is observed (an increase in the normalized resistance (III_A), followed by a decrease in the resistance (IV_A)). The above mentioned competition is seen in the parts of the cycle, where normalized resistance decreases (I_A and IV_A). This decrease is related to weak interactions of both molecules (NH_3 and H_2O) with the surface functionalities, which would eventually lead to the observed electrical outcome.

The decrease in the resistance at the very moment of the exposure of the chip to ammonia in humid air (I_A) followed by a much slower increase in the same parameter (II_A) may be explained by the occurrence of two simultaneous processes: fast surface interactions between ammonia/water molecules and the surface functional groups, and a much slower diffusion of the chemical species in the pore structure. The rapid resistance decrease is mainly caused by weak physical interactions (specific and non-specific), such as hydrogen bonding, dipole/dipole interactions and dispersive forces, which enhance electron transport across the small pores, through a charge hopping mechanism [50] (Figure 7C). The weak interactions, in which the non-bonding electrons of NH_3/H_2O participate, govern only the reversible sensing prior to which the chemical interactions of ammonia with the surface took place during the stabilization process. In the latter, bonding electrons are involved. An additional mechanism that could also lead to the rapid resistance decrease may involve a hole formation in the carbon matrix. This may be attributed to the partial oxidation of NH_3 to NO_2 , in the presence of superoxide ions, and/or the oxidation of the carbons' surface itself by the latter oxidant [37] (Figure 7C-1). The oxidizing effect of NO_2 towards thiols, bisulfides and amides has been reported in previous studies [46,51]. In the latter case nitramines and/or nitrosoamines were found to be formed as the oxidation products. In our case, the increased contribution of NO_x species, based on the XPS and potentiometric titration analysis, suggests the formation of similar products, therefore verifying that surface oxidation by NO_2 most likely took place. The formation of the holes and therefore the increase in the population of the charge carriers might have been caused by the electron withdrawing character of NO_2 (Figure 7C-1).

The second stage (Figure 7A- II_A) most likely involves a diffusion process and the re-equilibration of chemical species adsorbed or dissolved inside the pores. As a result of this, an

increase in the normalized resistance in much longer exposure times is observed. It is worth mentioning that the weak interactions, which initially caused the conductivity of the carbon chips to increase upon the ammonia exposure (I_A), are not involved in the electrical response any longer. Instead, the resistance increase is likely related to the electron donating character of both NH_3 and H_2O . In our previous study we showed that both carbons exhibit predominantly *p*-conduction type [37], which means that holes are the main charge carriers. Hence, exposure to ammonia which is an electron-donating gas would lead to their depletion, and therefore to a decrease in the conductivity. The depletion of the holes upon exposure to ammonia is illustrated in Figure 7C-2. When the same carbons were tested as ammonia sensors in dry conditions [37], it was found that ammonia exposure caused a rapid resistance decrease, followed by an increase in the same parameter upon air purging. Based on this, we can conclude that in moist conditions the second resistance change (increase- II_A), which was not observed in dry conditions, is likely related to the presence of moisture in the system. Since the latter mechanism of ammonia retention on the carbon surface (dissolution in water) is considered to be governed by rather weak adsorption forces [30], the adsorbate can be easily released upon purging the system with moist air. The removal of ammonia molecules upon moist-air purging is illustrated by an increase in the normalized resistance (Figure 7A-III $_A$). This increase can be also linked, once again, to the electron donating character of water. As more water molecules enter our system, they adsorb on the various O-, S- and N- surface groups (Figure 7C). These molecules act as nuclei for the formation of larger water clusters [27]. The connection of these clusters either across the pore or along the surface leads to the gradual pore filling, and eventually to the formation of a water layer/film [27]. Since the environment is acidic (the pH of C-AO is 3.53 and the pH C-BO is 4.03) [36], the adsorbed water molecules get ionized and form hydronium

ions (H_3O^+), which become the main charge carriers. As these ions get hydrated into H^+ and H_2O , the acceptance of a proton from an adjacent water molecule occurs, which in turn releases another H^+ (Figure 7C-3). This proton transport through the ionic conductivity (Grotthuss reaction) [26] would lead to the observed consequent resistance decrease (Figure 7A-III_A). Moreover, weak interactions of H_2O (mainly hydrogen bonding) with surface groups would also result in the same electrical outcome (resistance decrease).

Figure 7. (A): Typical response curves for both carbons, during an NH_3/air cycle, without prehumidification (B): Typical response curve for C-AO, during an NH_3/air cycle, with water being preadsorbed on its surface. (C): Sensing mechanisms that correspond to the electrical outcome of Figure 6A. (6C-1: hole formation due to the electron withdrawing character of NO_2 , 6C-2: hole depletion by electrons donated by ammonia, 6C-3: proton transport mechanism) (D): Sensing mechanisms that corresponds to the electrical outcome of Figure 6B – A high surface coverage of water molecules “blocks” those sites on the carbon’s surface, which would be otherwise available for weak interactions with ammonia, therefore leading to a limited charge hopping mechanism.

Comparison of the extent of the normalized resistance changes for both carbon chips when water is a part of the challenge gas, indicates that C-AO exhibits 5.5 times larger changes than C-BO (34.9% for C-AO vs 6.3% for C-BO) (Figure 3A). A reasonable explanation for these differences could be in the differences in the affinity of the carbon surface to adsorb water. Indeed, the comparison of the amount of water adsorbed on the surface of each sample, (8.9% on C-AO and 3.8% on C-BO), indicates C-AO as more hydrophilic compared to C-BO. This is also corroborated by XPS, where the % of O of C-AO is higher than that of C-BO (see Figure 6A). The chips made of C-AO also exhibits the largest electrical signal changes. Since C-AO is more accessible to water than is C-BO, more ammonia can be adsorbed through its dissolution, and therefore it can contribute more to the enhanced electrical signal. Furthermore, for the most hydrophilic carbon the contribution of water molecules to the electrical response of the sensor should be also greater. Another explanation of the difference in the extent of the normalized resistance changes could be related to the high concentration of superoxide ions (O_2^-) generated on the surface of C-AO. As such, a higher degree of hole formation upon the partial oxidation of NH_3 to NO_2 , and/or the oxidation of the carbon’s surface, would occur. Finally, the higher degree of carbon graphitization in the case of C-AO [36] also enhances the electron transport through the carbon’s matrix, and therefore it might contribute to the enhanced electrical responses.

Upon prehumidification, the extent of the normalized resistance changes decreased for both carbons (C-AO-EPM and C-BO-EPM). Moreover, differences in the electrical behavior are found (Figures 3B and 3C). In the case of C-BO (Figure 3C), the adsorption competition between water and ammonia molecules is seen once again, and the sensing response is similar to that when water was directly supplied to the system as a part of the challenge gas (6.30% for C-BO-EM vs 5.13% for C-BO-EPM). This is linked to the lower hydrophilicity of C-BO compared to that of C-AO, which limits the coverage of the carbon's surface with a water film, therefore leaving available sites for NH_3 adsorption. On the highly hydrophilic C-AO chip, on the other hand, preadsorption of water on the surface led to strongly suppressed changes in the normalized resistance due to the limited availability of surface functionalities, which would otherwise interact with the target gas (Figure 3B). The establishment of a dynamic equilibrium in the system decreased the competition effect. Here, a decrease in the normalized resistance is found upon exposure to ammonia (Figure 7B-I_B), which is followed by an increase upon moist-air purging (Figure 7B-II_B). The mechanism of this process is illustrated in Figure 7D. The initial conductivity increase may be attributed to weak interactions between NH_3 and available surface functional groups, and also to the proton transport mechanism through the abovementioned ionic conductivity. The observed further conductivity decrease is the result of the removal of weakly retained ammonia molecules.

Interestingly, the comparison of the electrical response of the C-AO chip in the moist target gas and that with water preadsorbed on carbon's surface, shows six times smaller signal changes in the latter case. This can be once again explained by the pore-filling process by water and ammonia dissolution in a water film. Since water molecules first fill the small pores of an adsorbent and then the larger ones [27,30], more water should be present in the larger pores

when prehumidification of the carbon is preformed than in the case of a direct exposure of the chip to moist ammonia stream. This observation is further supported by the changes in the pore volume of the C-AO carbon. A high surface coverage by water molecules likely causes “blocking” of those sites on the carbon’s surface, which would be otherwise available for weak interactions with ammonia, and therefore less marked electrical changes are recorded. The coverage with water molecules is illustrated in Figure 7D. For both carbon samples, a continuous resistance increase, throughout the sensing tests, is observed. A potential explanation for this is the charge transfer through the acid-base reaction of NH_3 with water to form aqueous ammonia, which is protonated forming NH_4^+ [52]. Another explanation for the continuous resistance increase may be related to the oxidation of the carbons’ surface upon ammonia exposure. Partial oxidation of the target gas by chemisorbed oxygen would lead to the formation of NO_2 , which as aforementioned can further oxidize the surface of the adsorbents and thus decrease their conductivity

4. Conclusions

The research presented on this paper shows the complex effect of humidity on the electrical properties of S- and N-containing nanoporous carbons, for the first time. A complex sensing mechanism was proposed based on the electrical behavior of the carbons and their extensive surface characterization. When the carbon chips were directly exposed to a moist stream of the carrier gas, a competition between water and ammonia for the same adsorption sites occurred, resulting in marked changes in the normalized resistance in the case of C-AO, compared to much smaller changes in dry conditions, reported previously [37]. This was not a case when prehumidification was applied, since smaller signal changes were observed for both carbons,

once again compared to dry conditions. The electrical behavior of the carbon coated chips upon ammonia exposure is governed by a fast surface reaction, followed by a much slower diffusion process in the pore structure and re-equilibration of chemical species adsorbed or dissolved inside the pores. The mechanisms that are involved in the electrical performance of the sensors include specific interactions of NH_3 and H_2O molecules with surface functionalities, proton transport through ionic conductivity, and hole depletion or formation in the carbon matrix itself, due to the electron donating or withdrawing character of $\text{NH}_3/\text{H}_2\text{O}$ and NO_2 , respectively. It was found that the pore-filling process by water molecules and ammonia dissolution in the formed water layer are primarily responsible for the sensing behavior of the carbons in moist conditions, and therefore the carbon affinity to adsorb water is considered as an important parameter. Upon prehumidification of the chips, a higher surface coverage by water molecules in the case of the most hydrophilic carbon, led to smaller changes in the normalized resistance, due to the limited interactions of NH_3 with the available surface functional groups.

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Captions to the Tables

Table 1. Change of normalized resistance $\Delta R/R_0$ [%] of the C-AO and C-BO carbon chips upon exposure to various ammonia concentrations in the moist conditions.

Table 2. Parameters of the porous structure calculated from the nitrogen adsorption isotherms.

Captions to the Figures

Figure 1. The experimental set-up.

Figure 2. Normalized change in a resistance for C-AO and C-BO upon their initial exposure to a humid gas stream (A) and a humid gas stream with two hours prehumidification (B and C).

Figure 3. Response curves for C-AO and C-BO upon exposure to NH_3 /moist air cycles (A) without prehumidification and (B, C) after prehumidification. For each concentration two sensing cycles are given. Dependence of the normalized resistance change on the various ammonia concentrations for the samples with (D) and without (E) prehumidification.

Figure 4. Ammonia breakthrough and desorption curves.

Figure 5. The pK_a distributions of the species present on the surfaces of the initial and exhausted carbons.

Figure 6. A) Content of elements; B-E) Surface concentration of the specific carbon, oxygen, nitrogen and sulfur groups. Due to the complexity of the species, the components of the N 1s core energy level spectra are referred to as N-1 (pyridines), N-2 (pyrroles/ammonia/amines/amides), N-3 (quaternary nitrogen and/or protonated amines) and N-4 (NH_4^+ and/or NO_2 species). Data for the initial carbons is taken from Ref. 36. Copyright 2014, with permission from Elsevier.

Figure 7. (A): Typical response curves for both carbons, during an NH_3 /air cycle, without prehumidification (B): Typical response curve for C-AO, during an NH_3 /air cycle, with water being preadsorbed on its surface. (C): Sensing mechanisms that correspond to the electrical outcome of Figure 6A. (6C-1: hole formation due to the electron withdrawing character of NO_2 , 6C-2: hole deletion by electrons donated by ammonia, 6C-3: proton transport mechanism) (D): Sensing mechanisms that corresponds to the electrical outcome of Figure 6B – A high surface coverage of water molecules “blocks” those sites on the carbon’s surface, which would be otherwise available for weak interactions with ammonia, therefore leading to a limited charge hopping mechanism.