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Ionic Liquids Filter for Humidity Effect Reduction on Metal Oxide Gas Sensor Response

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Abstract: The detection of gaseous pollutants such as Benzene, Toluene, Ethylbenzene and Xylene (BTEX) under real conditions requires working in a humid environment. It is well known that the humidity reduces the performances of gas sensors, particularly in terms of sensitivity. Ionic liquids (ILs) are a new class of solvent with attractive properties for the extraction of volatile organic compounds (VOCs) or gases. Moreover, the ILs are particularly interesting because of their recycling ability and without atmospheric pollution. Low concentrations of BTEX are detected with a tungsten trioxide (WO_3) thin film (50 nm) deposited by reactive RF magnetron sputtering on a transducer developed in our laboratory. Using a filter based on a mixed ionic liquid ([Bmim][Br]-[Bmim][PF_6]), we are able to detect 500 ppb of BTEX gases without a sensor sensitivity decrease with 50 % relative humidity.

Keywords: Gas sensor, Humidity removal, Tungsten trioxide, Ionic liquids based filters.

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1. Introduction

Air quality monitoring has become an important health and societal issue, since the European directive 2008/50/EC, particularly. Several toxicological and epidemiological studies have shown that air pollution causes respiratory problems, such as asthma, cardiovascular disease and cancer. Air pollution is estimated to be responsible for several hundred thousand premature deaths per year [1-2].

Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) are among the most harmful polluting gases due to their effect on health even at very low concentrations. BTEX is a useful suite to measure. In typical urban environments, there are a lot of VOCs present. Typical GC-MS analysis can resolve many BTEX, but 1) some of these may be below detection limits of the analysis and 2) the measurement is not obtained immediately. So metal oxide gas sensor can detect online very small BTEX concentrations. Moreover, the detection of gaseous pollutants under real conditions requires working in a humid environment. Indeed, ambient humidity significantly varies, according variations in weather, climate and temperature: the concentration of moisture in the atmosphere ranges from 6000 to 12000 ppm (at 1 atm and 25□) corresponding to 30 – 80 % relative humidity. The humidity often limits the performances of metal oxide gas sensors, particularly in terms of sensitivity. All metal oxide gas sensors are subject to interfering effects derived from water molecules that are still present in most of cases due to ambient humidity. Almost all types of metal oxides have a strong tendency to adsorb moisture to their surfaces, which leads to the degradation of the detection performances [3]. Because of the need of keeping reliably operating gas sensors, it is very important to eliminate or decrease the dependence of the response of oxide semiconductor gas sensors on humidity. Various strategies to reduce the influence of humidity have been considered:

1) Associate a p-type semiconductor, having a high affinity for moisture, with an n-type semiconductor oxide [4];

2) Make proper corrections on the sensor readings based on humidity and temperature variations[5];

3) Filter the gas upstream of the sensor to eliminate moisture [6].

Ionic liquids (ILs) have emerged as a promising green option to replace traditional organic solvents for gas separation in recent years because of their desirable properties like low vapor pressure [7], thermal stability [8], and tunable structures, which endow ILs the advantages of low energy consumption, less loss of absorbents and so on [9-11]. They have proven to be effective polar separation solvents with high selectivity and stability [12, 13]. Thus, these compounds have been successfully applied for heavy metal removal [14, 15], carbon oxide recovery [16, 17], humidity removal [18], and coupled with membrane processes [19, 20]. One of the most important characteristics of ILs is that they can be tailor-made designed for specific applications [21, 22]. IL's properties can be adjusted via chemical alteration of the cation and/or anion to produce application specific compounds [23]. This result in a large variety of ILs that can be adapted to given processes. The mainly cations used in the synthesis of ILs are ammonium, pyridinium, phosphonium and imidazolium. The structures of those cations are shown Fig. 1. These cations can be functionalized with alkyl chains (R_n) and they can be associate to common anions such as halides, BF_4^-, PF_6^-, and NTf_2^-.

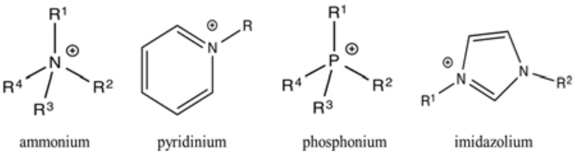


Fig. 1. The main cations of ILs.

The task specific ionic liquids (TSILs) [24] have been developed to enhance the selective solubility or/and recyclability [25]. The imidazolium based ILs can reduce air pollution, also they can increase the recycling and reuse potential [26]. More importantly, imidazolium based ILs show the high absorption capacity of water [27, 28]. 1-butyl-3-methylimidazolium bromide ([Bmim][Br]) was selected as the ionic liquid in this study because it is stable and recyclable [29].

The focus of this work is on the humidity removal which is one of the most important parameters affecting the sensor response. We developed an ILs based humidity removal filter reduces the relative humidity. Moreover, we demonstrated the possibility to detect low BTEX concentration (500 ppb) with 50 % relative humidity, without loss of the sensor sensitivity, using a WO_3 gas sensor with this filter upstream [30]. It is necessary to demonstrate that the ionic liquid only captures the humidity from air and does not affect the sensor response.

In Section 2, we describe the WO_3 microsensor, the test bench and the IL filter. In Section 3, we present and comment experimental results showing the effect of the IL filter on the detection of low BTEX concentration under 50 % relative humidity.

2. Material and Methods

2.1. Microsensor Design and Sensitive Layer

Our device is composed of an integrated Pt heater and Pt electrodes for the measurements, deposited by sputtering on a Si/SiO_2 substrate (Fig. 2) [31]. The sensitive layer of tungsten trioxide (50 nm) was deposited on the top of these electrodes, by reactive RF magnetron sputtering. After the sensitive layer's deposition on the Pt electrodes, the films were annealed at 743 K for 90 minutes in air to stabilize the chemical composition and the crystalline structure.

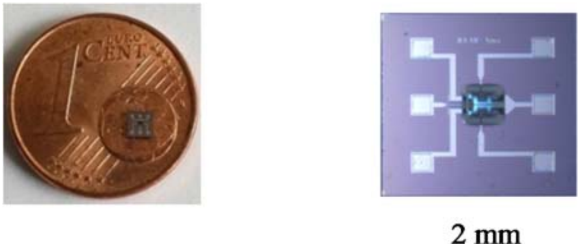


Fig. 2. Design of the sensor device [35].

WO_3 is n-type semiconductors with a large gap and oxygen vacancies. The main charge carriers are free electrons. The conductivity of this oxide depends on the composition of the surrounding gas atmosphere [32]. The physical phenomena for the gas detection are surface reactions between the oxygen ions adsorbed on the surface and the target gas. When the sensitive layers are under air, oxygen molecules come to be chemisorbed on the surface in ion forms $(O_2^-, O^- or\ O^{2-})$ [33] and electrons will be trapped on the surface of the sensitive layer. Thus, depletion layer will be created and the resistance of the sensitive layer will be changed. After the BTEX exposition, the oxydo/reduction reaction will take place on the surface of the sensitive layers as follows Eq. (1) [34]:

$$VOCs + O^{-} \rightarrow VOCs - O + e^{-} \qquad (1)$$

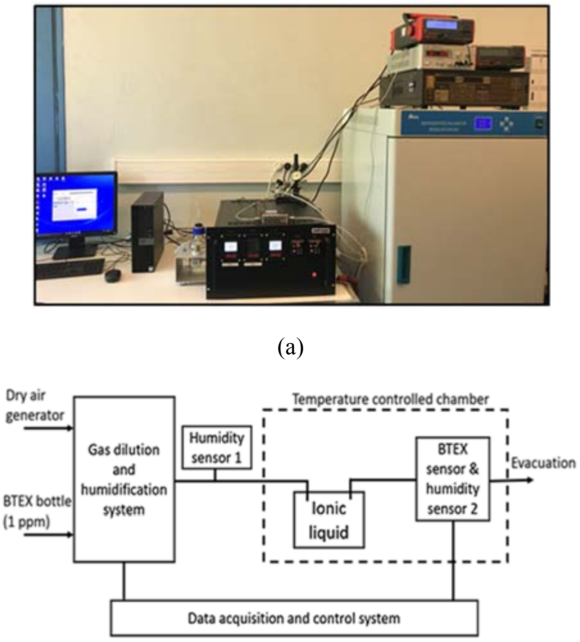
The Eq. (1) shows that an electron is released in the surface of the grain during the reaction, which will lead to the increase of the charge carrier density. This will induce the change of the depletion layer and so the decrease of the sensitive layer resistance allowing the detection of the target gas.

During all our studies, we used an operating temperature of 513 K. The electrical measurements were made under a constant gas flow of 100 sccm.

2.2. Test Bench for Electrical Characterization under BTEX Gases and Humidity

We used a test bench specially designed for the BTEX detection in the presence of different humidity levels (Fig. 3). It is composed of a gas dilution and humidification system that generates and output mixture at very low concentrations (1 to 500 ppb) with a variable humidity (0 to 90 %), an integrated test cell and an acquisition system to characterize the electrical responses of the gas micro sensor.

Humidity is generated starting from pressurized liquid water, which is vaporized through a microporous membrane. The water vapor is injected into the dry gas mixture by means of a proportional valve. This valve, controlled by a humidity sensor placed at the humidifier outlet, makes it possible to keep the hygrometry of the mixture constant. The vapor pressure is kept sufficient by heating and regulating the temperature of the vaporization cell. A second humidity sensor is placed at the output of the filter.



(a)

(b)

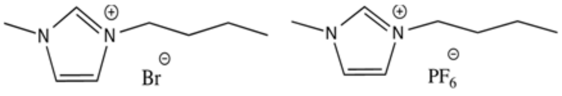
Fig. 3. Photo (a) and diagram (b) of the test bench.

2.3. Ionic Liquid Based Filter

To limit the effect of the humidity on the performances of metal oxide gas sensors, it is necessary to develop an ionic liquids based filter that only adsorb the water molecules from atmosphere without capturing the target gas molecules [36]. In this work, we consist of immobilizing ILs into support filter, which allows the amount of active phase needed for a given process to be minimized and greatly facilitates the recovery and reusability of ILs.

The [Bmim][Br] (The structure shows in Fig. 4(a)) has been selected because it is one of the most hygroscopic ILs. However, [Bmim][Br] is not a Room Temperature Ionic Liquid (RTIL) and the high melting point of [Bmim][Br] (80 □) is not allow to use it in a bubbling process. In this case, we mixed 10 % of [Bmim][PF_6] (The structure shows in Fig. 4(b)) into [Bmim][Br] to ensure the mixed ILs can be use in bubbling process. The [Bmim][PF_6] is one of RTIL with hydrophobicity. In addition, it is not interfering with the process of [Bmim][Br] absorption humidity. In order to eliminate the influence of a solid matrix or any other forms of support, the filter is made by bubbling the gas mixture into a glass container filled with mixed ILs (Fig. 5).

When the [Bmim][Br] was exposed on the wet air, it was found that it caught water vapors because the anions of IL (Br^-) and water molecules form H-bonding [37].



(a)

(b)

Fig. 4. The structures of (a) [Bmim][Br] and (b) [Bmim] [PF_6].

Fig. 5. The ionic liquids based filter and bubbling process.

3. Results and Discussion

3.1. Influence of Wet Air on Sensor Response to BETX

Almost all metal oxides have a greater or lesser sensitivity to moisture, which often leads to the degradation of their detection performance. This influence of moisture is well known and is widely described in the literature [38].

To study the humidity influence on the sensor responses, the sensors were exposed to 500 ppb of BTEX for 4 minutes (Fig. 6) under dry air and wet air (50 % RH). The sensor response was calculated using the relation (2):

$$Sensor\ response\ (\%) = \left(\frac{R_{air} - R_{gas}}{R_{gas}}\right) * 100, \qquad (2)$$

where R_{air} is the sensor resistance in air before gas exposure and R_{gas} is the sensor resistance in presence of BTEX.

Under dry air, the sensor response to 500 ppb of BTEX is 24 %. The introduction of 50 % of relative humidity in the atmosphere reduces the sensor response to 12 %. The sensor response is divided by 2 under 50 % of relative humidity.

This behavior is well known and has been already reported in the literature. Several hypotheses have been made about this behavior [39]. Firstly, the adsorption of the water molecules leads to a decrease in the chemical adsorption of the oxygen species on the surface of the metal oxide [40]. Secondly, The BTEX molecules compete with the water molecules to react on the same adsorption sites [41]. In both cases, the introduction of relative humidity in the atmosphere leads to a decrease of the sensor response.

The result showed that the sensor is vulnerable to the errors occur due to the presence of humidity. Thus, a humidity removal device is developed in order to minimize the effect of humidity.

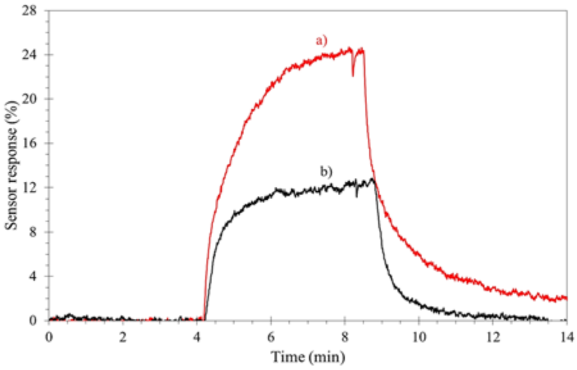


Fig. 6. Sensors response under 500 ppb of BTEX, a) Dry air (0 %), b) wet air (50 %) without IL filter.

3.2. Influence of Ionic Liquid Based Filter

In the previous section, it was shown that the effect of humidity of the sensor response. Therefore, a humidity removal filter is used here to practically eliminate the humidity influence on the sensor response. We placed the IL filter upstream to the sensor and we exposed the sensor to 500 ppb of BTEX for 4 minutes (Fig. 7) under wet air (50 % RH). As the gas goes through the IL filter, the humidity of the gas is lowered, and hence the humidity effect on the response is eliminated. In Fig. 7, we can observe that when the IL filter is placed upstream the sensor, the response to 500 ppb of BTEX remains 25 %. Hence, with this filter, we keep the BTEX detection performance of our sensor, even in presence of 50 % of relative humidity in the atmosphere.

The main objective of this work being to validate the filter ability to trap water vapor, we first chose to work with a 50 % humidity rate, which is considered as a good reference for gas sensors tests. Now that we have shown the performance of this type of filter, it will be interesting to study, in future experiments, its behavior at higher humidity levels. This will help to understand at which humidity the sensor response significantly declines.

Furthermore, Fig. 7 shows that the response of the BTEX sensor with the filter inserted into the gas flow is slightly higher and has a larger slope compared to the response under dry air. This behavior is reproducible. It may be related to the high viscosity of the ionic liquid, which causes pressure and flow rate variations at the gas sensor. Further experiments are needed to validate this hypothesis.

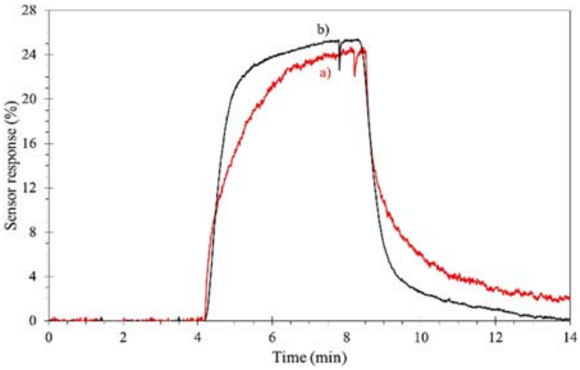


Fig. 7. Sensor response under 500 ppb of BTEX, a) Dry air (0 %), b) wet air (50 %) with IL filter.

4. Conclusion

In this work, we proposed a new solution to protect metal oxide gas sensors from the influence of humidity. We show the possibility to detect low BTEX concentrations under wet air with a WO_3 gas sensor associated with a filter based on ionic liquids. A low-cost and reliable humidity removal filter is used to eliminate the effect of humidity on a metal oxide gas sensor. The developed filter reduced the level of humidity and stabilized it using environmental friendly compounds. We also demonstrated that the ionic liquid based filter didn’t disturb the BTEX detection. These results show that the proposed humidity removal significantly enhances the performance of the sensor.

Further work is in progress to study the behavior of the IL filter under high level of humidity and to insert the IL into a solid matrix to make a more convenient filter.

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