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Optimization of Sensing Layers Selection Process for Relative Humidity Sensors

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Abstract. Electronic devices designed for environmental monitoring have gained an increasing importance in the last years. Parameters such as *relative humidity* (RH), temperature, pressure, acceleration and speed, measured by devices such as RH, temperature, pressure, and motion sensors, are at the core of the efforts for improving the environmental conditions. The employment of such devices in complex sensing systems enable their use in IoT (*Internet of Things*) applications, which is of paramount importance for an in-time and appropriate reaction to adverse environmental phenomena. Given all these, the need to design sensors with improved sensing performance, such high sensitivity, reduced cross-sensitivity and low response time, emerges. The aim of this paper is to introduce the *Hard-Soft Acid Base* (HSAB) concept as a valuable investigative tool to explain, to a certain extent, the increased sensitivity and selectivity experimentally demonstrated by different used *metal oxides* (MOX) and their nanocomposites to relative humidity. Based on literature data, six different case-studies of RH detection by sensing layers employing metal oxides and related composites, are highlighted and investigated in terms of HSAB theory. To support the thesis that the HSAB principle can be a useful criterion and can be taken in account when either selecting a suitable gas sensing layer (in particular, for RH detection) or optimizing his functional response, we will build our argumentation on three reasons:
1) strong RH detection capabilities of MOX layers classified as hard acids according to the HSAB theory;
2) strong ethanol, ammonia and trimethylamine detection capabilities of MOX layers classi-

fied as hard acids;
3) the significant role played by dopants classified as hard acids in the performance of MOX-based RH sensing layers.

Key-words: Humidity Sensor; Metal Oxide; Hard Soft Acid Base.

1. Introduction

Sensors have gained increased importance in many of day-to-day activities, being present in homes and offices, hospitals and hypermarkets, leisure places and official buildings, etc. They're an essential part of the *Internet of Things* (IoT), a network of physical devices, able to connect and exchange data within the Internet infrastructure. The IoT sensors market was evaluated at more than 4.5 billion USD in 2017 and it is expected to reach 22.48 billion USD by 2023 [1]. Environmental monitoring is one of the applications that greatly benefits from environmental monitoring. Pressure, temperature and flow sensor, accelerometers, magnetometers, gyroscopes are frequently used as IoT sensor solutions. Last, but not least, *relative humidity* (RH) sensors are key components in such networks devices [2].

Moisture is present at different concentrations in most surroundings. As a consequence, humidity is one of the most frequently monitored environmental physical parameter and is of great importance in various areas of environmental control, in both domestic and industrial applications. Amongst the applications where RH sensors are essential, one could mention monitoring of the environment in buildings, cooking control for microwave ovens, intelligent control of laundries, etc.

From the perspective of commercial and industrial applications, one can mention the textile and paper industry, medical field (respirators, incubators, sterilizers), pharmaceuticals (synthesis and quality control of drugs), the wood processing industry, the automotive industry (oil humidity control, engine assembly lines), agriculture (dew prevention, cereals storage, soil moisture control) [3, 4]. At the same time, the chemical industry (dryers, chemical gas purification, and furnaces), electronics (wafer processing) and meteorology are areas where RH monitoring is a sine qua non requirement. Thus, manufacturing RH sensors has gained significant attention, becoming a priority over the last 20 years [5].

Many principles and methods were described in the literature for measuring RH [6 - 12] and different types of materials have been tested as RH sensing layers. Besides polymers [13 - 17], nanocarbon materials [18, 19], polyelectrolytes [20, 21], inorganic salt and their composites [22, 23], sensors employing *metal oxides* (MOX) as sensing layers were also widely used in the last decades. This is a consequence of their outstanding features, such as low cost and increased flexibility in manufacturing, rapid response and recovery times, simplicity of their use and high RH sensitivity. Pre-transition MOX, like Al_2O_3, MgO, transition-metal oxides (Fe_2O_3, Cr_2O_3, etc.) and post-transition-metal oxides (SnO_2, etc.), are important candidates for humidity sensing [24]. Intensive efforts were devoted to improving their sensitivity, selectivity, thermal and chemical stability. Thus, a plethora of these materials and their composites were tested as RH sensing layers, yielding different selectivity, sensitivity, hysteresis, and response time. Considering the influence of different factors on the RH sensing properties of MOX, different mechanisms and models were proposed to coherently explain their sensing properties [25].

However, none of these models can fully explain the RH sensing capabilities of different MOX layers. Why some oxides are more sensitive towards humidity than others? Why some oxides are selective and can discriminate between humidity and certain types of gases, but cannot discriminate between humidity and other types of gases? These issues (and not only these) are still debatable

In this paper, we propose Pearson's *Hard-Soft Acid-Base* (HSAB) concept as a possible investigative tool to explain, to a certain extent, the sensitivity and selectivity of different MOX and of their nanocomposites to RH. In order to support our claim HSAB can be a valuable selection tool when choosing the most suitable gas sensing layer (in particular, for RH detection) we will build our argumentation-based on three reasons:
1) strong RH detection capabilities of MOX layers classified as hard acids according to the HSAB theory;
2) strong ethanol, ammonia and trimethylamine detection capabilities of MOX layers classified as hard acids;
3) the significant role played by dopants classified as hard acids in the performance of MOX-based RH sensing layers.

2. MOX-Based Gas Sensing Layers Selection HSAB Theory

We presume that direct and distinct interaction of metal oxides cations and water molecules can have tremendous importance on getting accurate information about the sensing mechanism and performances of the MOX-based RH sensors in terms of the sensitivity, selectivity, response time, etc. In order to understand this assumption, we employ the HSAB theory [26].

This theory is primarily a qualitative concept and was developed by Ralph Pearson in the early nineteen sixties; this concept is useful in predicting the stability of different compounds, possible metal-ligand interactions in complexation reactions, the predilection of some chemical species to interact with other species, specific reaction mechanisms [27, 28]. The HSAB concept has proven to be a beneficial investigation tool in many fields of chemistry and biochemistry, such as: medicinal chemistry, toxicology [29], computational quantum chemistry [30], corrosion [31], quantum dot functionalization and design of quantum dot solar cells [32, 33], TiO_2 functionalization [34], adsorption phenomena [35], tribology [36].

In the last decade, the HSAB theory was used in sensing research and development. Based on this theory, many sensing layers were synthesized and used in sensors based on different working principles and detecting species such as carbon dioxide [37-44], nitrogen dioxide [45], sulphur dioxide [46], ethanol [47], mineral acid [48], ammonia [49], hydrogen sulphide [50], oxygen [51, 52], benzene [53].

The HSAB concept operates with Lewis bases and acids; a molecular entity donating a pair of electrons is classified as a base, while a molecular entity accepting a pair of electrons is classified as acid. Pearson categorizes Lewis' bases and acids into hard, borderline, and soft. Hard bases are highly electronegative, have a high HOMO energy level, while hard acids have empty orbitals in their valence shells, small ionic radii, high positive charge, empty orbitals in the valence shell and high LUMO energy level. Simultaneously, soft acids possess low positive charge and large ionic radii, while soft bases have large atoms with high polarizability intermediate electronegativity [54]. Borderline species have an intermediate character, between hard and soft species. To be classified as soft, hard or borderline, a Lewis base or acid does not have to possess all the above-mentioned properties. Examples of hard, soft and borderline acids and bases are given in Table 1.

The large electronegativity differences between hard acids and hard bases lead to strong ionic interactions, while the electronegativities of soft acids and soft bases are almost the same, thus their interactions are predominantly covalent.

Table 1. Examples of hard, soft and borderline acids and bases

	Hard	Borderline	Soft
Bases	**H_2O**, PO_4^{3-}, CH_3OH, C_2H_5OH, $C_2H_5O^-$, O^-, ClO_{4-}, N_2H_4, CH_3COO^-, NH_3, acetone, Me_3N, H_2N-$(CH_2)_4$-NH_2, H_2N-$(CH_2)_{5-}NH_2$, CO_3^{2-}, Cl^-	Aniline (C_6H_5-NH_2), C_5H_5N (pyridine), N_2, Br^-, N_{3-}	RCN, SCN^-, C_2H_4, RSH, CO, R_3P, R_3As, $(RO)_3P$, CN^-, R_3P, C_6H_6, I^-
Acids	Al^{3+}, Sm^{3+}, Ga^{3+}, K^+,	Fe^{2+}, Bi^{3+}, Ni^{2+}, Zn^{2+},	Cu^+, Pt^{2+}, Ag^+, Au^+,
	In^{3+}, La^{3+}, Gd^{3+}, Li^+,	$B(CH_3)_3$, Pb^{2+}, NO^+, Cu^{2+}	Pd^{2+}, trinitrobenzene, chloranile
	$B(OR)_3$, Mg^{2+}, Ce^{4+}, Na^+, Fe^{3+}, Co^{3+}, Ti^{4+}, Cr^{3+}, Zr^{4+}		

The HSAB theory elaborates that a hard base prefers to bind to a hard acid to give ionic complexes, whereas a soft base prefers to interact to a soft acid to give covalent complexes. Correspondingly, a borderline base tends to bond to a borderline acid. From the HSAB theory perspective, water is classified as a hard base. Thus, according to the HSAB theory, hard acid species (Table 1) are virtually suitable candidates for RH detection. Indeed, by investigating the literature, we found that most of the metal oxides exhibiting good RH detection performance (regardless of being dielectric materials or n-type or p - semiconductors) can be classified as hard acids according to HSAB theory. Six such cases are analyzed below.

3. Hard Acids MOX-Based RH Sensing Layers

A) The RH sensing layer is based on a MOX containing cations classified as a hard acids

SnO_2, ZrO_2, TiO_2, ZrO_2, β-Ga_2O_3, SiO_2, Al_2O_3, CeO_2 are all MOX employing hard acid cations. They were all reported in the literature as being suitable for RH detection (Fig. 1).

Kuang *et al.* developed a high-sensitivity RH sensor based on a FET device [55]. The sensing layer consists of single SnO_2 nanowire (250 nm diameter), synthesized by chemical vapour deposition. The conductivity of the nanowire increases after exposure to the moisture. The sensor exhibits a fast and linear response to RH variations in the air. The nanodevices are highly sensitive and have relatively good reproducibility. Taking into account room temperature sensor operation, the explanation offered by authors is that the pre-adsorbed oxygen on the surface of the SnO_2 nanostructure has been displaced by competitive water adsorption. In terms of the HSAB theory, this displacement can be explained as being a consequence of water (a hard base) molecules preference to bond with hard Lewis acid sites (Sn^{4+} cations employed by the single SnO_2 nanowires).

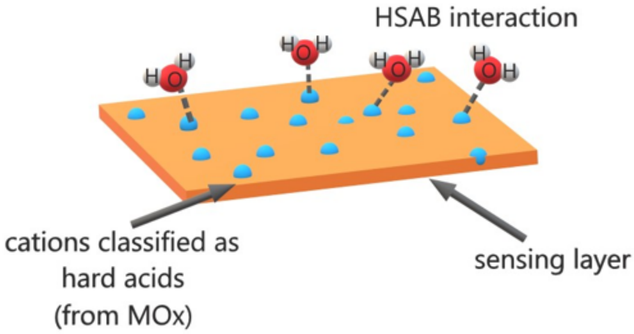

Fig. 1. Hard Acids MOX-Based RH Sensing Layers and their interaction with water molecules.

Wang *et al.* used size-controlled ZrO_2 nanorods for RH sensing at 25°C [56]. The RH sensing material was synthesized via a hydrothermal process, using NH_4F as a mineralizer. The sensing capability of the ZrO_2 was evaluated by measuring the impedance response to the humidity change at 100 Hz. The sensor exhibited both high sensitivity and significant linearity, its impedance varying with three orders of magnitude when RH increasing from 33% to 95%.

Juan *et al.* reported on manufacturing RH sensor using monoclinic gallium oxide (β-Ga_2O_3) nanowires as a sensing layer [57]. The n-type semiconductor nanowires were synthesized via a vapour-liquid-solid mechanism by heating a GaN/sapphire template. It was found that the conductivity of the β-Ga_2O_3-based sensitive film decreased monotonically when RH was increased from 30 % to 95 %. The sensor exhibited good linearity with a hysteresis value of 5,4 %. Apart from the author's explanation of the sensing mechanism (*i.e.* the release of trapped electrons, water dissociation process, hydrogen peroxide formation), the HSAB principle can be again employed, as the water vapours (hard based) adsorb onto the surface of β-Ga_2O_3 nanowires, replacing the ionized oxygen previously adsorbed.

Khanna *et al.* developed a model for explaining the variation of the surface conductivity of a porous anodic Al_2O_3 film with RH changes [58]. According to the authors: "*At low humidities, a phonon-induced electron tunnelling is postulated between donor water sites; at high humidities protonic conduction dominates*". In both cases, the HSAB type of interactions seems to play a fundamental role. Chemisorption of water-vapour molecules on the surface, the formed hydroxyl and the adsorption of O^{2-} species on the Al^{3+}, with the liberation of protons, are in fact relevant interactions between the hard acid Lewis sites (Al^{3+}) and the hard bases Lewis sites (HO^-, O^{2-}).

It is worth pointing out that the above-mentioned sensing material (Al_2O_3) can be found in nature much more often than its corresponding sulphide (Al_2S_3) due to a phenomenon which again can be explained by the HSAB concept: Al^{3+}, a hard acid, prefers to bind to O^{2-}, a hard base, rather than to S^{2-}, which is a soft base [59].

Zhang *et al.* developed a humidity sensor with high sensitivity, rapid response and good linearity using TiO_2 nanotubes as sensing layers [60]. The thin film was prepared by anodic oxidation and calcined at different temperatures. The sample annealed at 600° C exhibited the best performances. When varying RH between 11% and 95%, the resistance of sensor decreased by almost two orders of magnitude.

Fu *et al.* reported on an RH sensor employing CeO_2 nanowires as sensing layers [61]. The sensor showed excellent response and recovery time (approx. 3 s). Its resistance decreased exponentially with increasing RH. According to the authors, the driving force of the humidity sensing is water chemisorption on the surface of the Ce nanowires. They also associate the strong electric field induced around the surface of ceric oxide (which enhances water ionization and decreases the resistance) to the properties of Ce^{4+}. These cations have high positive charge, small ionic radius and induce high charge density on the surface of the nanowires. At the same time, these are also the most significant properties of hard acids. It is, therefore, reasonable to conclude that the large surface-to-volume ratio of the nanowires has an important contribution to the sensor performance, but the key factor for the remarkable RH properties of the sensor seems to be the strong interaction between a hard acid (Ce^{4+}) and hard base (H_2O).

In conclusion, no matter the type of conductivity of the metal oxides employed as RH sensing layer (dielectric, n-type semiconducting, p-type semiconducting), no matter its type of preparation (nanotubes, nanowires, thin film, thick film), the Lewis interaction, introduced by the HSAB theory, plays a major role in explaining the sensing mechanism between MOX and RH (water adsorbed molecules trigger all reactions) and decisively influences the sensor performance.

B) The sensing layer is based on a MOX containing cations classified as hard acids, doped with inorganic salt also containing cations classified as hard acids.

Examples of MOX with hard acids cations, doped with inorganic salts with hards acids cations include LiCl-doped porous silica [62], LiCl doped TiO_2 electrospun nanofibers [63], KCl-doped SnO_2 nanofibers [64]. In all the situations, doped MOX exhibited better RH sensing performance compared to non-doped MOX.

For instance, in the case of the KCl-doped SnO_2, the addition of alkali ions (hard acids, according to the HSAB theory) yielded a device with outstanding sensing characteristics: fast response time (6 s) and recovery time (7 s), excellent reproducibility, stability, and linearity. When varying the RH from 11% to 95%, at room temperature, the impedance decreased by five orders of magnitude (from 10^8 to 10^3 Ω). These are performing better than those shown by RH detectors based on non-doped SnO_2 sensing layers.

In another relevant example, doping with Li^+ ions (a hard acid) a ZrO_2–TiO_2 ceramic layer increased its RH sensitivity by two orders of magnitude and also improved its linearity [65].

C) The sensing layer is a nanostructured composite material, comprising a MOX with cations classified as hard acids and a semiconducting organic polymer.

TiO_2 nanoparticles / polypyrrole [66], polyaniline / CeO_2 [67], TiO_2 nanowires / Nafion [68], nano-anatase/P_3HT [69] are examples of nanostructured composite materials, comprising a MOX with cations classified as hard acids and a semiconducting organic polymer. In all the cases, the MOX plays an important role and improves the RH detection performance of the sensing film. For instance, a hybrid nano-anatase-poly (3-hexylthiophene)-based RH sensor exhibits five fold higher sensitivity and a hysteresis reduced to one third compared to a pristine semiconducting organic polymer-based RH sensor.

D) The sensing layer comprises two types of metal oxides, both containing cations classified as hard acids.

Examples of layers comprising two types of MOX, both containing cations classified as hard acids, include TiO_2-SnO_2 thin films [70], TiO_2/SiO_2/TiO_2 [71], MgO/KCl-SiO_2 composites [72], Ga_2O_3/SnO_2 [73]. All the above-mentioned nanocomposites exhibit remarkable RH detection performance. For example, the TiO_2-20 wt. % SnO_2 film shows high RH sensitivity, exhibiting three orders of magnitude change in the resistance when varying RH from 20 to 90 %.

E) The sensing layer comprises two types of metal oxides, both containing cations classified as hard acids.

Examples of layers comprising two types of MOX, one of them containing cations classified as hard acids, include ZnO/TiO_2 core/shell nanorod [74] CeO_2/ZnO nanoarray [75], ZnO-SiO_2 composite [76], Al_2O_3-doped ZnO nanocomposite [77]. The first two examples require special attention. ZnO/TiO_2 core/shell nanorods, synthesized by the hydrothermal method of zinc oxide nanorods cores followed by the deposition of anatase TiO_2, exhibit excellent sensing properties. Complex impedance analysis shows that the capacitance varies from 10^1 to 10^6 pF over a relative humidity range of 11 % – 95 % at room temperature. As we see, the TiO_2 shell (hard acid) ensures water adsorption and enhances humidity sensitivity. As in the case ZnO/TiO_2 core/shell nanorods, ZnO nanowires are uniformly coated with a layer of CeO_2 nanoparticles. According to the authors, Ce^{4+} ion, with small ionic radius and four positive charges (hard acid, according to HSAB) is responsible for water adsorption and outstanding sensing capabilities.

F) The sensing layer is a nanostructured composite material, comprising a MOX with cations classified as hard acids and a hydrophilic polymer.

Example of RH sensing nanostructured composite materials, comprising a MOX with cations classified as hard acids and a hydrophilic polymer, include polyvinylic acid (PVA) and polyethylene glycol (PEG) with TiO_2 nanoparticles [78], SiO_2 and poly-[3-(methacrylamino)-propyl]-trimethyl ammonium chloride [79] and SiO_2 with poly-(2-acrylamido-2-methylpropane sulfonate) [80].

4. Hard Acids MOX-based Ethanol, Ammonia and Trimethylamine Sensing Layers

As presented above, a plethora of sensing layers based on MOX was designed, manufactured and tested for RH detection, yielding different sensitivity, selectivity, and response time performance. In most cases, the cations of the employed MOX were classified as hard acids.

Besides water, there are several other compounds, which are categorized as hard bases in accordance with the HSAB theory, which can be detected by means of hard acids MOX-based sensing layers. Among these, one can mention ammonia, dimethylamine and biogenic amines (trimethylamine, cadaverine, and putresceine), other oxygen donor species, such as ethanol, carbonylic compounds (formaldehyde, *i.e.*) [81]. According to the HSAB theory, MOX classified as hard acids, which are also sensitive to RH, should act as a sensing layer for other types of hard bases. Indeed, literature data confirm that hard acids MOX, such as SnO_2 [82, 83], TiO_2 [84], In_2O_3 [85], α-Fe_2O_3 [86], and Ga_2O_3 [87], are appropriate sensing layers for ethanol detection, hybrid Co_3O_4/SnO_2 core-shell [88] and Cr_2O_3 [89] were employed for ammonia sensing, SnO_2/In_2O_3 hetero-nanofibers have been shown to be sensitive to formaldehyde [90], while trimethylamine was detected at low temperature using a TiO_2 membrane nanotubes [91].

At the same time, the use of MOX as RH sensing layers in chemiresistive sensors, FET nanodevices [55], fiber optic-based sensor [92, 93], surface acoustic wave sensor [94], bulk acoustic wave sensor [95], supports the idea that, regardless of the type of sensor and its principle of detection, the type of strong interaction between hard acids MOX and water molecules triggers all types of sensing processes.

5. Hard Acids Dopants Role in Increasing RH Detection Performance of MOX-based Sensing Layers

When investigating the RH sensing performance of different types of Fe_2O_3-based composites, Li^+ ions were found to be a highly effective factor for increasing the sensitivity of the sensor, particularly at low values of RH [96]. This result can be due to the high polarizing effect of Li^+ ions (charge/ volume ratio =1.11). At the same time, this effect is an attribute of hard acids. For comparison, Au^{3+} (which is a soft acid, with a charge/ volume ratio of 0.28) exhibits worse RH detection performance.

In another example, when investigating the RH detection properties of K^+ and La^{3+} co-doped nanoporous TiO_2-10 mol % SnO_2 thin films, it was found that the ions (which are both hard acids) have a strong role in improving the RH sensing [97].

6. Conclusions

The paper proposes the *Hard-Soft Acid Base* (HSAB) theory as a valuable tool for understanding the behaviour and RH sensing performances of MOX-based sensing layers. Six case studies of water (a hard base) detection by means of different types of sensors employing hard acids MOX were discussed from the perspective of this theory. Furthermore, to emphasize the importance of the HSAB concept when selecting sensing layers suitable for gas detection, other supporting evidence was presented:

- The use of hard acids MOX-based sensing layers for the detection of other gases, apart from RH, which are classified as hard bases;
- The essential role played by hard acid dopants in the RH detection of MOX-based sensing layers.

Obviously, the interaction between MOX and water molecules is not the only factor influencing the overall performance of an RH sensor employing MOX-based sensing layers. Other factors, such as grain size, porosity, surface area, thickness, deposition method, types of additives, crystallographic facets, temperature and presence of other gases influence the sensing process. At the same time, more in-depths calculations regarding electronegativity, HOMO and LUMO energy levels and local hardness are necessary for better understanding of key RH sensing properties of MOX and their nanocomposites.

However, taking into account the significant amount of literature data on the RH detection employing hard acids MOX-based sensing layer, one can conclude that this concept can be essential when choosing and designing a gas sensing layer and explaining the performance of a gas sensor.

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