Humidity sensor based on zeolite for application under environmental conditions

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A B S T R A C T

This work evaluates two different zeolite-based humidity sensors. In the first case, interdigital capacitive sensors (IDC-S) were fabricated on the surface of Al_2O_3 ceramic substrates, using electrode gaps of 20 μm, and were coated with films of LTA-type (Lind Type A) zeolite with Si/Al ratio of 1.28. Complex impedance spectroscopy (IS) was used to measure the sensor response, which was related to the change in capacitance of the interdigital electrodes and, in turn, to the electrical properties of the zeolites. The zeolite-based sensors were characterized in terms of the effects of changes in humidity and temperature on the sensor response.

The results showed that this sensor provided detectable capacitance changes at very low water contents (up to 300 ppmv of H_2O in N_2), at temperatures ranging from 25 to 100 °C, and was therefore suitable for moisture trace measurements.

In the second part of the work, evaluation was made of a humidity sensor based on ZSM-5 (Zeolite Socony Mobil - 5) zeolite. Interdigital capacitive sensors were fabricated on the surface of Al_2O_3 ceramic substrates, with electrode gaps of 20 μm, and were coated with films of ZSM-5. The results showed that the sensor was capable of good performance (detection limit of ~7.32% RH) and was suitable for use under a broader range of environmental conditions (~39% RH - 96% RH), compared to sensors based on other materials such as polyimide (detection limit of 20% RH) and TiO_2 (detection limits from 10% to 30% RH).

1. Introduction

The measurement of humidity is becoming increasingly important in various fields of human activity, ranging from simple domestic purposes to sophisticated industrial applications [1]. Humidity measurements are essential to avoid spoilage of pharmaceuticals, fuels, and chemicals, as well to control manufacturing and storage conditions. Humidity is a key determinant of weather and climate, and affects global climate change (since water vapor is a greenhouse gas). Environmental pollution due to the emissions of toxic substances into the atmosphere has also contributed to the interest in humidity monitoring. Humidity measurements assist in minimizing the operational costs of air-conditioning systems and are required for the monitoring of solar UV irradiation [2]. Various

humidity sensing methods are commercially available, but most (around 75%) are based on capacitive techniques, with measurement of impedance change [3]. Interdigital capacitive sensors (IDC-S) are based on planar capacitors with the electrodes in a comb-like interlocking configuration [4]. Interdigital electrode structures have been described for diverse applications in the field of gas sensing. They possess useful features such as the ability to be used at a wide range of frequencies, control of signal strength by changing the dimensions, multiple physical effects in the same structure, and simplified modeling in two dimensions when the aspect ratio of the electrode length to the sensor spatial wavelength is large. They can be manufactured using various inert substrates and different processes, and are compatible with microfluidic systems.

The patent of N. Tesla, issued in 1891, is probably the earliest example of an interdigital electrode design [5,6]. Materials that have been studied for use as sensitive layers include porous amorphous silicon carbide (PASiC) [7], gold-coated nanoparticles (AuNPs) [8], graphene oxide (GO)/poly(diallyldimethylammonium chloride) (PDDA) [9], zinc oxide (ZnO) [10], aluminum oxide (AlO)

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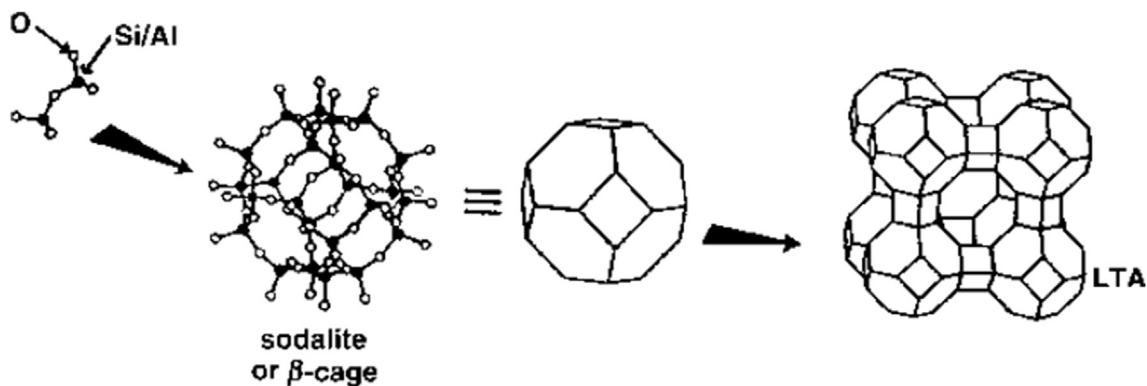E-mail addresses: gpalcantara2@uem.br, gpamaster@gmail.com (G.P. Alcantara).

Fig. 1. Construction of zeolite LTA framework with sodalite or β cages, from a pair of TO$_4$ tetrahedral (adapted from Ref. [19]).

[11], silicon carbide nanowire (nw-SiC)/silicon nanoporous pillar array (Si-NPA) [12], bismuth phosphate (BiPO$_4$) [13], mesoporous silicas (SBA-15 and SBA-16) [14], and polypyrrole films [15]. In this work, zeolite film was selected as the sensing layer, because zeolites with different size pores are available, which can assist in enhancing the selectivity of the device. Furthermore, it has been shown that changes in the electrical properties of zeolites due to the adsorption of guest molecules can provide the basis for different potential sensor applications [16].

In previous work, we compared the sensitivities of zeolite-based chemical sensors with three different electrode structures, namely conventional interdigitated electrodes (IDE), serpentine electrodes (SRE), and ring-shaped electrodes (RSE) [17]. In this paper, we describe the development of a sensor device based on LTA-type (Linde Type A) zeolite for the sensing of low levels of humidity (moisture trace measurement). We also evaluate a humidity sensor based on ZSM-5 (Zeolite Socony Mobil - 5) zeolite, operated under environmental conditions, covering a higher humidity range. Here we are interested in validating the use of zeolite as humidity sensor showing that, despite using few samples, several measurements and characterizations were made. Thus, the full characterization with statistical study, will come after new rounds of development. The sensor responses are analyzed considering the adsorption process of the analyte and the influence of temperature changes.

Section 2 of this work describes the characteristics of the zeolite frameworks. Section 3 provides a brief description of the IDC-S structure used in the experiments. The materials and methods of fabrication, deposition, and measurement are provided in Section 4. The results are discussed in Section 5, and conclusions are drawn in Section 6.

2. Zeolites

Zeolites are crystalline aluminosilicates of group IA and IIA elements such as sodium, potassium, barium, magnesium, and calcium. Their physical structures are porous, with interconnected cavities containing metal cations and water molecules. The fundamental structural unit of a zeolite is a tetrahedron with four oxygen atoms surrounding a relatively small silicon or aluminum atom.

Structurally, the zeolite framework consists of an assemblage of tetrahedral SiO$_4$ and AlO$_4$ units connected together in various regular arrangements by means of shared oxygen atoms, forming an open crystal lattice containing pores of molecular dimensions into which guest molecules can penetrate. The zeolite framework is open, containing channels and interconnected voids filled with exchangeable cations and water molecules [18].

The structural formula of a zeolite is usually expressed in terms of the crystallographic unit, as follows:

$$M_{x/n}\left[(AlO_2)_x(SiO_2)_y\right]\cdot wH_2O \qquad (1)$$

where M is the cation of valance n, w is the number of water molecules, and the y/x ratio (Si/Al) usually has values in the range 1–5, depending on the structure. The sum $(x + y)$ is the total number of tetrahedra for each unit cell. The portion within the square brackets represents the framework composition [19].

Fig. 1 shows the construction of the zeolite LTA framework with sodalite or β cages, based on a pair of TO$_4$ tetrahedra. In the case of a completely siliceous structure with tetrahedral Si, as depicted in Fig. 1, silica (SiO$_2$) with a neutral charge is created. On the other hand, when aluminum atoms with charge of +3 are introduced into the zeolite structure to replace some of the silicon atoms with charge of +4, a negative charge is created within the framework [20].

In order to maintain neutrality of the overall zeolite framework, after the introduction of Al into the silica framework, extra-framework cations (which can be inorganic or organic) electrostatically bound to the host are allowed to move along the channels. The amount of Al within the framework can vary over a wide range, with Si/Al ratios ranging from 1 to ∞, and as the Si/Al ratio increases, both the hydrothermal stability and the hydrophobicity also increase [21].

3. IDC-S structure

Fig. 2 shows a model representing the IDC-S devices coated with zeolite and undergoing the process of adsorption of the analyte. It can be seen there are four interdigitated capacitive structures with gold electrodes. The zeolite is deposited over the entire surface of the device, resulting in a change in capacitance when the adsorption of analyte occurs.

4. Experimental

4.1. Materials

As shown in Fig. 3, the samples of IDC-S devices with electrode gaps of 20 μm were constructed on alpha phase alumina substrates (3M Inc., 96%) with dimensions of 25 mm × 25 mm × 0.6 mm, average grain size of 3–5 μm, and maximum surface roughness of 6 μm. The IDC-S devices used in this work were availed from a previous work [22]. In order to ensure an even distribution of