Chapter 9

An Exploratory Study on the Potential of Zeolite P-Based Materials for Sensing Applications

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Abstract The synthesis, characterization and electrical properties of zeolite P-based material have been reported. It was verified that thick films can be deposited on ceramic substrates forming a homogeneous and porous structure, making easy the fabrication of thick film-based sensors. The structural properties of these materials revealed moreover an ideal environment for gas or vapor adsorption. Sensing properties of resistive devices fabricated using zeolite-P/MWCNTs composites have shown a rapid response and high sensitivity to relative humidity.

9.1 Introduction

Zeolites are crystalline, microporous hydrated aluminosilicate containing exchangeable alkaline and alkaline earth cations in their structural frameworks. Due to the high absorption properties of micropores, zeolite-based materials have received great attention for sensing applications. Moreover, they can selectively absorb specific chemical species depending on their shape and size, thus enhancing sensor selectivity.

Several chemical sensor device typologies have been reported taking advantage of the zeolite frameworks properties [1–4]. Generally, zeolites exhibit no measurable electronic conductivity since they have a wide electronic band gap of

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several eV. On the other hand, since mobile cations are present within the zeolite framework that may hop from one binding site to the next, zeolites exhibit ionic conductivity, allowing their use in impedance sensors. The adsorption of chemical species on zeolite results in a measurable mass change. As a consequence, a great variety of sensor studies investigate the application of zeolite layers onto piezoelectric microbalances (QCM) or surface acoustic wave (SAW) devices. In both cases, the mass change is transformed into a frequency shift of the piezoelectric resonator.

Moving from these facts, we have initiated a study aimed to investigate novel zeolite-based materials as sensing layer for the development of chemical sensors, focusing our interests on zeolite P-based materials. The zeolite P class includes a series of synthetic zeolite phases which may be in cubic configuration (also termed B or Pc) or tetragonal configuration (also termed P1). Recently we prepared a novel zeolite P-based material (Z-PM) by a patented hydrothermal treatment starting from a pumice mine waste [5]. This zeolitized-P material showed a high content of crystalline zeolite P in Na^+ form, Si/Al atomic ratio of about 2.2, surface area of 34 m^2/g and micropore area 3.6 m^2/g. As these structural properties could provide an ideal environment for molecular adsorption, an exploratory study was undertaken on the feasibility of using porous zeolitized-P materials for sensing applications.

9.2 Experimental

Zeolite P-based materials can be obtained by a structural conversion from amorphous natural sources or by chemical synthesis. We recently synthesized a novel zeolite P-based material (Z-PM) by a patented hydrothermal treatment starting from a pumice mine waste, by extracting as much silica as possible by a sodium alkali aqueous solution in hydrothermal conditions and by rinsing the un-extracted residue with water up to neutral pH [5].

Synthetic zeolite P has been prepared according the following procedure. In brief, a solution “A” was prepared dissolving a mixture of sodium aluminate (20% Al_2O_3, 20% Na_2O, 60% water) and NaOH in water under stirring at 348 K. A solution “B” was prepared dissolving sodium silicate (30% SiO_2, 12% Na_2O, 58% water) in water. The solution “A”, after a preheating treatment, was poured into a reactor kept at 368 K. When solution “B” was added slowly (about 5 min) to the aluminate solution, a silico-aluminate gel was instantaneously formed. The gel was maintained at 368 K under reflux for 5 h. After this time, it was filtered on a buckner and repeatedly washed with 200 ml of water until a pH of 12.5 was reached. The synthesized zeolite P was finally heated at 383 K in a oven for 8 h.

The characterization of the synthesized Z-PM material was carried out by XRD, SEM-EDX, TEM surface area and porosity measurements. An aqueous suspension of the Z-PM material, in the presence of sodium metasilicate ($Na_2SiO_3 \times 5H_2O$) acting as a binder, was used for the deposition of Z-PM thick films on the

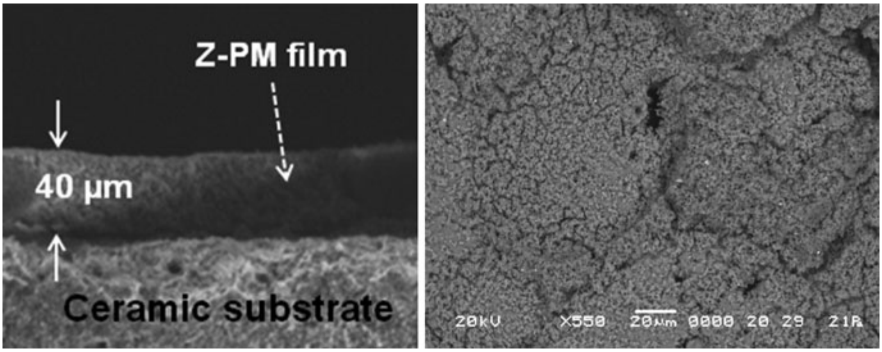

Fig. 9.1 SEM micrographs showing, respectively, the cross-section and the surface of the thick film on the ceramic substrate

interdigitated ceramic substrate of resistive-type sensors. The electronic conductivity of the Z-PM material was modulated by adding to the above aqueous suspension the suitable amount of multiwalled carbon nanotubes (MWCNTs).

9.3 Results and Discussion

Initially, we carried tests aimed to investigate the deposition of thick films of the zeolitized materials on ceramic interdigitated substrates. Practically, the deposition of thick films was accomplished by screen printing from aqueous slurry solutions. In order to exploit better performances, the film must adhere strongly to the substrate, maintaining the same time a relatively high surface area. To improve the adherence of the film on the surface of the ceramic substrate, an aqueous solution of sodium metasilicate has been used as a binder.

SEM micrographs reported in Fig. 9.1 show, respectively, the cross-section and the surface of the Z-PM layer (about 40 μm thick) on the ceramic substrate. It can be noted the good thickness homogeneity and the porous structure of the film.

Humidity sensing tests have been carry out on the fabricated resistive devices. However, as expected, pure Z-PM films were extremely resistive, with resistance values in a range not measurable by our instrumentation.

Then, to decrease the resistance of the sensing layer, Z-PM material was mixed with different loadings of MWCNTs. The excellent electrical conductivity ($>10^5$ S/m for multi-walled carbon nanotubes) should make them suitable candidates in preparing zeolites-CNTs composites, which may offer high electrical performances unattainable by pure zeolites.

Preliminary sensing tests have shown the promising characteristics of the Z-PM material used in combination with MWCNTs for monitoring humidity by resistive sensors. The transient response of the sensor to different relative humidity variations is reported in Fig. 9.2.

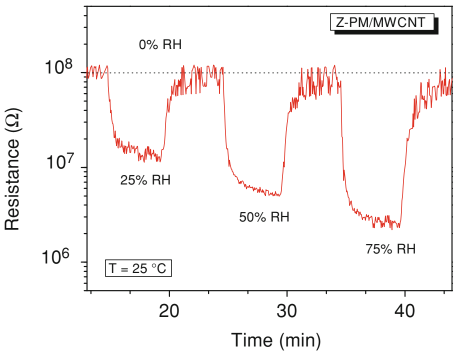

Fig. 9.2 Transient response of the sensor to different relative humidity variations

Starting from an initial conditions of RH = 0, a strong decrease of resistance was observed going towards higher RH. Moreover, the response is well reversible. It was clearly evinced that both the response and the recovery times were fast. Specifically, the response time as humidity changed from 0 to 75% RH, and the recovery time as humidity changed from 75 to 0% RH, was about 90 s.

9.4 Conclusion

A novel resistive humidity sensor has been designed by using a natural zeolitized-P material, showing well characteristics of sensitivity and reversibility. In order to exploit further the potential of these materials, we also will explore the possibility to synthesize zeolite P films directly on the surface of a piezoelectric QCM or SAW devices, to fabricate novel types of humidity and gas sensors. By using cation exchange properties of Z-PM, in a suitable cation form and able to quickly exchange with other cations [6, 7], could open further prospects for the development of selective chemical sensors species also in liquid phase.

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