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DIELECTRIC SENSITIZATION OF ZEOLITIC IMIDAZOLATE FRAMEWORK-8 (ZIF-8) NANOPOWDER

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Abstract: Metallo-organic complexes are a class of materials that are increasingly used in sensory applications. Zeolitic imidazolate frameworks (ZIFs) are their subclass that are topologically isomorphic with zeolites. The porosity of the crystals and their chemical structure, as well as their thermal and chemical stability, make some of these materials (ZIFs) very suitable for making sensors. The large specific area of micro and nano particles is an important parameter for sensor applications. Despite the fact that the dielectric characterization of powders in the RF domain was neglected in scientific works, this method can have great practical importance. This paper presents the results of the dielectric characterization of the ZIF-8 nanopowder in the frequency range of 24 Hz to 24 KHz. The results indicate that the presence of evaporation of water, ethanol and methanol leads to major changes in the dielectric permittivity of ZIF-8 nanopowder.

Keywords: ZIF, nanopowder, dielectric permittivity, vapors, sensor.

1. INTRODUCTION

The dielectric response of powders is strongly influenced by the effects of the particle surface. Interaction between particles and their interactions with the gas molecules surrounding them can dominate the dielectric response of the powdered material in relation to the dielectric response of that material as a result of its continuous structure. This suggests that the knowledge of the electrical properties of the material in the powder state can be used for gas detection, but also for photoelectric applications, such as for example dye-sensitized solar cells DSSCs [1,2].

Zeolithic imidazolate frameworks (ZIFs) are substances that belong to a group of metallo-organic complexes. ZIFs are topologically isomorphic with zeolites and they are characterized by a large diversity in composition, framework types and properties [3,4]. The applications of these materials are numerous. Their role as catalyst in chemical reactions [5] can be mentioned, while their crystalline structures are shown to be suitable for the separation of gases [6]. Zeolitic imidazolate framework-8 (ZIF-8) is a chemically robust and thermally stable material, and zinc metal centers tetrahedrally coordinated to 2-methylimidazole groups build up its chemical structure [3]. The crystal structure of ZIF-8 is characterized by a sodalite zeolite-type structure with large cavities (11.6 Å) and small pore apertures (3.4 Å) [3].

The two main objectives of this article are the presentation of a method of dielectric powder characterization and the dielectric characterization of ZIF-8 nanopowder (26 nm) in the frequency range of 24 Hz to 24 KHz in the presence of the evaporation of water, ethanol and methanol. The method of dielectric characterization of powders in the radiofrequency domain is not common in scientific works, the reason being the problem of the quality of powder contacts with electrodes, whereas in the case of high frequencies (microwave) and relatively non-conductive materials, this problem does not exist. On the other hand, the use of high frequencies is generally not good for sensor applications because measuring signals are greatly affected by various disturbances such as small changes in cell geometry or external radio interference. This article describes a simple setup for the dielectric characterization of powders in a lower radiofrequency domain where the powder is in contact with only one electrode, while air separates it from the other electrode. A very simple calculation of the value of the dielectric

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powder permittivity on the basis of the mentioned geometry was used without a more detailed analysis of other possibilities. ZIF-8 is a hydrophobic material, but the results indicate that the dielectric permittivity of the ZIF-8 nanopowder can vary widely depending on the presence of the evaporation of water, ethanol and methanol.

2. EXPERIMENTAL

2.1. Materials

ZIF-8 nanoparticles were synthesized by an isotremal procedure in methanol at a temperature of 50 °C. A detailed description of the synthesis is given in the article by C-W. Tsai and E.H.G. Langner 2016 [7], the external surface area of the nanoparticles is 336 m^2g^{-1} and the mean diameter is 26 nm. For the powder sensitization, there were used: 1 x distilled water; ethanol and methanol (99% Merck).

2.2. Method

The dielectric characterization was carried out in a measuring cell in which the powder is in contact with the bottom electrode, while between the powder and the upper electrode was air. Also, the two lateral sides of the cell were open to allow the flow of outer air into the cell. An approximation was carried out according to which the measuring cell consists of two parallel-connected capacitors, C_1 – capacitance of powder (ZIF-8) and C_2 – capacitance of air, as illustrated in Figure 1. Based on the aforementioned approximation, permittivity of the powder is calculated on the basis of the expression: $\varepsilon` = 1 + (\varepsilon`_{eff} - 1)\cdot V\cdot \rho/m$, $V = 25x25x2$ mm^3 – cell volume, $\varepsilon`_{eff}$ – effective diel. permittivity of the ZIF-8/air mixture in the cell, capacity of the cell: $C = \varepsilon`_{eff} \cdot \varepsilon_o \cdot S/d$; S – surface of electrodes; $d = 2$ mm distance between electrodes; $\rho = 0.95$ g/cm^3 i $m = 20 \pm 1$ mg are the respective density and mass of ZIF-8 nanopowder samples.

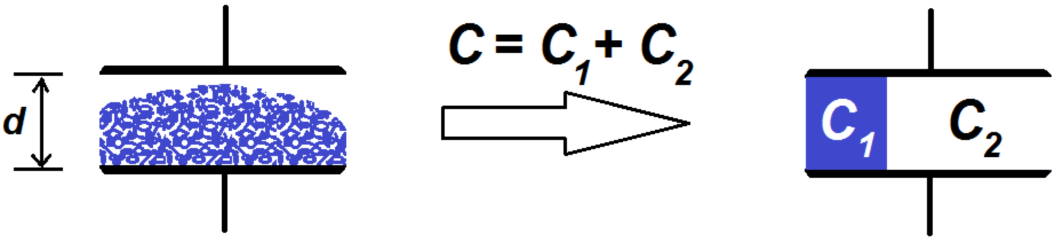

Figure 1. The approximation of powder capacitance in the cell.

Changes in dielectric permittivity due to the presence of evaporation were carried out in such a way that the samples were first conditioned under relative humidity conditions (*RH*) of 20%. Measurements were started at the moment when the appropriate fluid was introduced into the cell (water, ethanol or methanol). Measurements lasted until the AC conductivity components reached saturation values (saturation of the vapor).

Dielectric spectroscopy measurements were performed on a Hameg 8118 instrument in a frequency range between 24 Hz and 24 kHz ($U_0 = 1$ V) at room temperature (22 ± 0.3 °C) and a pressure of 850 mbar (85 kPa).

3. RESULTS

Changes in the dielectric permittivity of ZIF-8 nanoparticles due to an increase in humidity over time from $RH = 20\%$ to $RH = 100\%$ are shown in Figure 2a. The most pronounced increase in the dielectric permittivity, in this humidity range, was noted at the lowest measuring frequency, $f = 24$ Hz. The changes in the dielectric permittivity of the ZIF-8 nanopowder became less pronounced with an increase in the frequency. The corresponding conductance, shown in Figure. 2b, was obtained without applying the approximation mentioned in the experimental section (Figure 1). In contrast to capacitive conductivity (dielectric permittivity), the changes of which relatively well describe the increase in humidity in the measuring cell, the in-phase AC conductivity (conductance) shows irregular changes during the increase in humidity and therefore this quantity cannot be suitable for sensor applications in this case.

The conductance of the ZIF-8 nanopowder, which over time has been exposed to ethanol and methanol vapors, also exhibit irregular changes during an increase in the vapor concentration, similar to the results in Figure 2b, and they are not shown here.

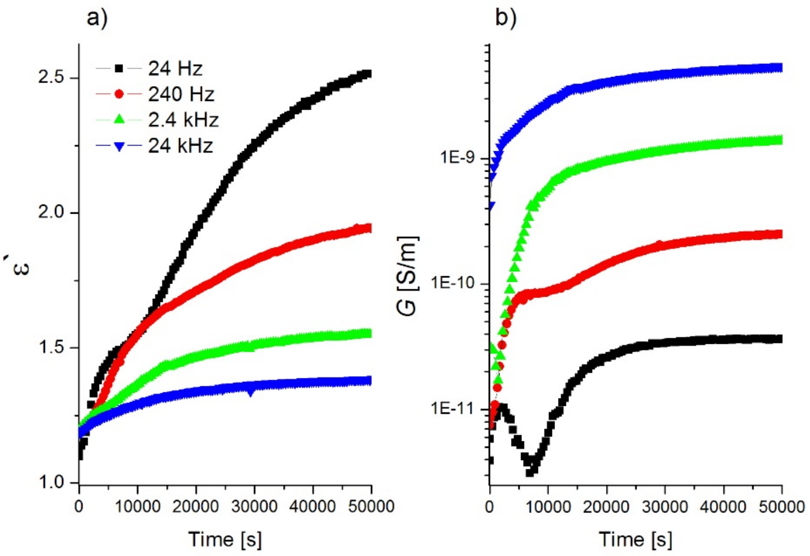

Figure 2. Changes in dielectric properties of ZIF-8 nanopowder with an increase in relative humidity from 20% to 100% over time, a) dielectric permittivity and b) conductance.

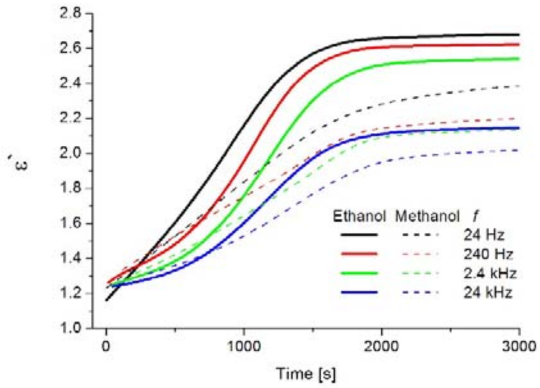

Figure 3. Dielectric permittivity of a ZIF-8 nanopowder exposed to vapors of ethanol (full line) and methanol (dashed line).

The increase in the dielectric permittivity of the ZIF-8 nanopowder over time due to an increase in the evaporation of ethanol and methanol in air is shown in Figure 3. Similar to the case of water vapor (Figure 2), the largest increase in dielectric permittivity was obtained at the lowest measuring frequency *f* = 24 Hz. The increases in dielectric permittivity due to the presence of ethanol vapors are greater than those caused by methanol vapors, but in both cases the saturation values of dielectric parameters have been reached about ten times faster than in the case of exposure to vapors of water.

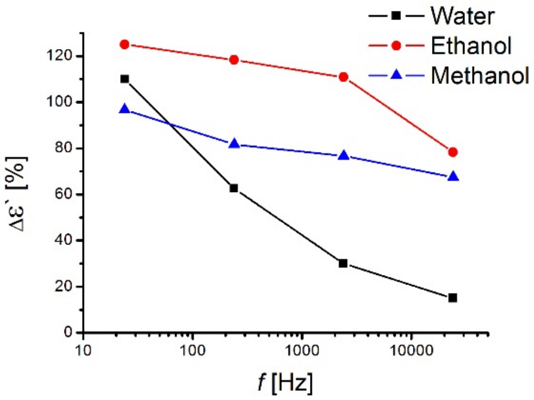

Figure 4. The increase in the dielectric permittivity of the ZIF-8 nanopowder which have been achieved in saturated vapors of water, ethanol and methanol in the air, and calculated in relation to the dielectric permittivity at RH = 20%.

Figure 4 shows the frequency dependence of the saturation values of the dielectric permittivity of ZIF-8 nanopowder calculated as an increase in relation to the dielectric permittivity at *RH* = 20%. As can be seen in Figure 4, the largest increase in the dielectric permittivity of the ZIF-8 nanopowder is achieved in the evaporation of ethanol. Changes in the dielectric permittivity of the ZIF-8 nanopowder due to the presence of these vapors become less pronounced with an increase in the measurement frequency, and this phenomenon is particularly pronounced in the case of ZIF-8 nanopowder under water vapor.

4. CONCLUSION

This study describes the effect of the evaporation of water, ethanol and methanol on the dielectric properties of ZIF-8 nanopowder. Both components of the AC conductivity of the ZIF-8 nanopowder, capacitance and conductance, exhibit a high sensitivity to the said vapors. The dielectric permittivity of the ZIF-8 nanopowder may be increased more than 100% due to the presence of saturated vapors of water, ethanol and methanol in air relative to the dielectric permittivity of ZIF-8 nanopowder conditioned at a relative humidity of 20%. The dielectric sensitivity of the ZIF-8 nanopowder to these vapors decreases with increasing measurement frequency.

Bearing in mind that the ZIF-8 material is hydrophobic, the method of dielectric spectroscopy of powders at lower radio-frequencies (24 Hz - 24 kHz) proved to be very suitable for the potential sensor applications of this material.

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ДИЕЛЕКТРИЧНА СЕНЗИТИВИЗАЦИЈА НАНОПРАХА ЗЕОЛИТСКЕ ИМИДАЗОЛ СТРУКТУРЕ 8 (ЗИФ8)

Сажетак: Метало-органски комплекси су класа материјала која налази све већу примену у изради сензора. Зеолитске имидазол структуре (ЗИФ) су њихова потккласа која је тополошки изоморфна зеолитима. Порозност кристала и хемијска структура, затим термална и хемијска стабилност, чине да су неки од ЗИФ материјала веома погодни за израду сензора. Велика специфична површина микро и наночестица важан је параметар за сензорске примене. Упркос чињеници да је диелектрична карактеризација прахова у радиофреквентном домену запостављена у научним радовима, та метода може да има велику практичну важност. У чланку су презентовани резултати диелектричне карактеризације ЗИФ8 нанопраха у опсегу фреквенци од 24 Hz до 24 KHz. Резултати указују да присуство испарења воде, етанола и метанола доводи до великих промена у диелектричној пропустљивости ЗИФ8 нанопраха.

Кључне речи: ЗИФ, нанопрах, диелектрична пропустљивост, испарења, сензор.

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