Sensing Device for Breath Rate Monitoring Fabricated by using Geomorphic Natural Clinoptilolite

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Abstract: The possibility of using slices of geomorphic clinoptilolite of natural origin in the fabrication of humidity sensors for personal spirometers and breath rate monitors has been investigated. These water sensors have shown to be fast-responding and therefore adequate for detecting all minimal variations in the ventilation activity. This type of sensor could allow to count the number of breathing events during a time interval (breath rate) and in combination with fast datalogging systems could be potentially exploited to draw accurate spirograms of the hexalation process. Signal detection can be based on the current intensity increase or on the voltage-drop, which follows to breath exposition, and the approach based on voltage-drop has shown to be very sensitive.

1. INTRODUCTION

Zeolites have tremendous potentialities in biomedical applications [1-3], indeed they are used as liquid-phase adsorbents for uremic toxins in blood purification by dialysis [3,4], carriers for drug and gene delivery [5], enzyme mimetics [6], potent hemostatics (due to their capacity to adsorb water) [7], scaffolds for bone formation (in combination with polymers) [8], glucose adsorbent for diabetes mellitus extra therapy [9], adjuvant for vaccines [5], etc. These biomedical applications of zeolites are mostly related with their porous character and their ion-exchange properties. Since zeolites are also ionic conductors [10], and their electrical conductivity is strictly depending on the environmental humidity at a given temperature, another very promising field of application for these materials could be as sensor in biotechnology and medicine. Respiratory rate is a vital sign and it has been identified as a key predictor of potentially serious clinical events [11]. In particular, the respiratory rate is an important indicator of severe derangement in many body systems, and not just the respiratory system. Zeolite-based water sensors [12,13] can be used for fabricating continuous respiratory rate counters that provide an early indication of health deterioration. There are various non-invasive respiratory monitors on the market, however recently a new monitor has been introduced that measures the respiratory rate based on the humidity of the exhaled air [14]. In particular, a humidity sensor, placed on a facemask, measures water vapor of the exhaled air. The derived humidity

signal is electronically transmitted to a monitor that calculates respiratory rate on a breath-to-breath basis using for example a 3-breath averaging algorithm (surprisingly, there is a lack of accepted standards for these devices, for example, there is no agreed convention regarding averaging time, or breaths, or accuracy). In addition, zeolite-based water sensors could be useful for achieving graphical displays of breath flow, known as spirograms, whose shape is used by physicians to differentiate between lung abnormalities. Therefore, zeolite-based low-cost spirometers could be used to measure a variety of parameters in real-time and these devices are extremely useful for thorough respiratory assessment and to detect mild diseases.

The possibility of using zeolite as moisture sensor is based on the fact that high siliceous zeolites (i.e., hydrophobic zeolites, Si/Al>5), like natural clinoptilolite, have a scarce tendency to adsorb water vapor on their surface because they have a hydrophobic nature. In fact, the equilibrium constant for water adsorption has been calculated by using a kinetic approach and it resulted of $2.9 \cdot 10^{-1}$ at room temperature [15]. The exact amount of water adsorbed on the clinoptilolite surface depends on the humidity of the environment where the mineral is located and it is as high as the environmental humidity; in other words, the water present on the stone surface is in dynamic equilibrium with water contained in the environment. Since, during adsorption, cations combine with water molecules, and therefore the number of mobile charges (hydrated monovalent cations, KOH_2^+ in the present case) is directly proportional to the number of adsorbed water molecules, it is possible to monitor the humidity variations in the environment where clinoptilolite is

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located by measuring the electrical conductivity of this material. When the surface conductivity is measured (i.e., the sensor electrodes are placed on the zeolite slice surface), the sensor response to the external stimulus (humidity change) is very fast and promptly reversible because surface cations are selectively involved in the electrical transport.

Here, mechanically robust zeolite-based sensors have been fabricated simply by slicing the geomorphic stone. The geomorphic aluminosilicate mineral has a high-density [16], since it has been compressed over millions of years until its density approaches that of a single zeolite crystal (typical bulk density ~2.7gcm^{-3}). Natural clinoptilolite has essentially no macroporosity (only micro and mesoporosity are present) and therefore it can be envisioned as a solid block of zeolite with regular and uniform 7.4Å pores [17]. Zeolite of natural origin is much more convenient than synthetic zeolites for sensor fabrication, because synthetic zeolites are produced in form of powders and require to be pelletized by introducing a polymeric binder which is electrically insulator. The used natural clinoptilolite has been characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and infrared spectroscopy (FT-IR) and the ability of the fabricated sensor to detect human breathing has been in vivo tested.

2. EXPERIMENTAL

The electrical sensors were produced by directly slicing the geomorphic natural clinoptilolite stone by a diamond saw (electrical mini-grinder, Vigor) and painting two electrodes with a thickness of ca. 0.5mm on the slice surface by using silver pant (ENSON, EN-06B8). Such a two-lead measurement involves a small contact resistance due to the silver-zeolite interface, that slightly reduces the sensor sensitivity. Since electrodes are placed on the stone surface, only cations (hydrated monovalent cations, that is KOH_2^+) near the surface are involved in the electrical transport

phenomenon. Different strategies can be used to detect the conductivity change associated with sensor during water vapour adsorption. The simplest approach is based on micro-current intensity measurement by using the a.c. micro-ammeter contained in a digital multimeter (DMM). In this approach a sinusoidal voltage signal of 20V$_{pp}$ and 5kHz was used to bias the two electrodes. The applied sinusoidal voltage was generated by using a direct digital synthesis (DDS) function generator (GW Instek SFG-1013) and the effective current intensity was measured by a 100kHz bandwidth, true-RMS micro-ammeter (Brymen BM869s) connected in series with the zeolite sample. Owing to the relatively low frequency of the current signal and its very low intensity, the use of a DMM results much more convenient than the use of a digital storage oscilloscope (DSO), combined with shunt or current probe. Time-resolved current intensity measurements were recorded by the digital multimeter datalogging system (Brymen BU-86X). Electrical measurements were performed in air at room temperature (20°C).

Since clinoptilolite breath sensors required in service very fast current intensity reading, some large bandwidth, true-RMS, datalogging DMM have been tested at low resolution, to verify the possibility to record the measured micro-current data at very high speed. To decrease sample reactance due to the electrode polarization, it is required to use sinusoidal signal of current with a frequency higher than 1kHz (typically, 5kHz) and therefore the minimum bandwidth that was required for the DMM was 10kHz. The Uni-Trend DMM model UT71D is a 10kHz bandwidth digital multimeter, able to measure effective micro-current intensities (true-RMS) with a resolution of 10nA at a rate of 9Sa/s, in low resolution mode (i.e., digital multimeter set at 4,000 count mode). This type of handheld DMM has shown to be very adequate for the clinoptilolite sensor data acquisition, and further DMM models tested for monitoring the sensor response are given in Table **1**.

Table 1:   Characteristics of the Data Logging, True-RMS Digital Multimeters used as Microammeter

DMM model	Type	Company name	Bandwidth (kHz)	Resolution (nA)	Sampling rate (Sa/s)
UT-71D	Handheld	Uni-Trend	10	10	8-9
BM869s	Handheld	Brymen	100	10	5
UT-171B	Handheld	Uni-Trend	100	10	4
UT61E	Handheld	Uni-Trend	10	10	2
VC650BT	Benchtop	Voltcraft	10	10	1

Since the above described approach based on micro-current intensity measurement by an a.c. micro-ammeter is not very sensitive, some alternative strategies for the sensor signal monitoring have been developed. One method is based on connecting an a.c. voltmeter (or an a.c. micro-voltmeter) in series with the zeolite sample, in this case the voltmeter input impedance works like a shunt and an ideal a.c. voltmeter results connected in parallel with this shunt. Due to the very high resistance of the shunt, even p-Amperes can be measured by this approach. A further very convenient detecting method for zeolite-based humidity sensors has been described in the literature [18]. In this method the clinoptilolite-based humidity sensor is biased by a very low power a.c. generator (e.g., the LCD back panel driving signal with a flipping polarity of 3-5V, depending on the device model) and the sensor response is detected in form of voltage drop at sensor electrodes. Lower is the generator power, higher the sensor sensitivity results.

The morphology of natural clinoptilolite samples, the Si/Al ratio and type of contained ions were established by SEM/EDS analysis (FEI Quanta 200 FEG microscope). The crystalline phases present in the natural zeolite sample were identified by XRD (X'Pert PRO, PANalytical). The presence of water adsorbed in the natural clinoptilolite samples was qualitatively investigated by infrared spectroscopy (FT-IR, Nicolet used in ATR mode).

3. RESULTS AND DISCUSSION

The morphological/structural characterization of the natural clinoptilolite used for sensor fabrication provided important information on all those factors affecting the operation of this type of device. Therefore, in order to optimize the device design, a preliminary material study was performed by standard material characterization techniques.

As visible in the SEM-micrograph shown in Figure **1a**, the natural clinoptilolite slice has essentially no macroporosity, and it can be envisioned as a solid block of zeolite with uniform microstructure. However, two different types of porosities are contained in this natural clinoptilolite mineral: the primary porosity is related to the presence of a regular array of microscopical channels (nanotubes with a lume of 7.4Å) in the crystal lattice of the mineral and it is referred as microporosity; the secondary porosity is related to the fine-graining structure of this mineral which involves an inter-grain boundary space and it is referred as mesoporosity. In fact, the mineral is made of lamellas with a uniform thickness of 40nm, face-to-face arranged to form block-shaped aggregates. The morphology of the single lamellar crystal contained in the mineral can be clearly visualized by observing the fractured surface of the natural clinoptilolite (for example, observing fragments of a crushed clinoptilolite sample) by scanning electron microscopy (SEM) (see Figure **1b**). Such lamellar texture of natural clinoptilolite causes the presence of an inter-grain boundary space, which is responsible for a diffusion-controlled transport mechanism during the water molecule adsorption process [19]. Owing to this morphology, three contributions to electrical transport are possible for zeolites (i.e., surface, bulk and inter-granular electrical conduction), and these contributions have been experimentally separated in order to study each one of the related mechanisms by limiting the
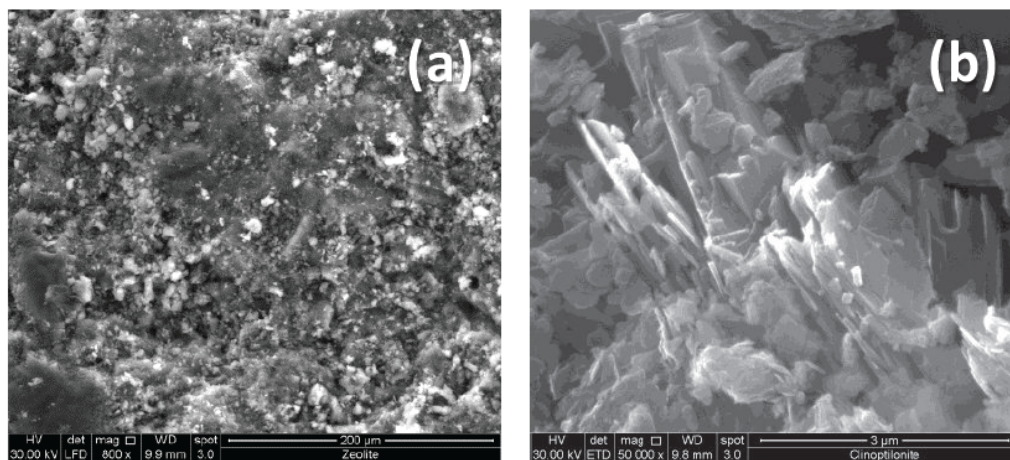

Figure 1: SEM-micrographs of the simply sliced clinoptilolite surface (**a**) and fragment surface in the mechanically treated mineral (**b**). The mechanical treatment causes delamination of the mineral polycrystalline structure pointing out its lamellar texture.

electrical measurements to the surface and by controlling the sample hydration conditions [15].

Further information on the clinoptilolite of natural origin useful for designing the breath sensor were provided by SEM microanalysis: the natural zeolite has a high siliceous nature (hydrophobic zeolite) in fact the Si/Al atomic ratio is 5.4 (see Table **2**). The EDS approach for the Si/Al measurement (that is, Si/Al=at.%Si/at.%Al) is much easier to apply than that based on FT-IR [20], which provides a Si/Al value of ~4 according to the absorbance value given in Table **3**. The charge carrier is K^+; indeed K^+, Ca^{2+} and little amount of Mg^{2+} and Fe^{3+} are the only cations contained in the sample (thus proving that this sample is clinoptilolite-K) and only K^+ can move by hopping among the free nucleophylic areas present in the framework, originated because of the Ca^{2+}, Mg^{2+}, and Fe^{3+} cation presence. This type of clinoptilolite is very convenient for electrical application since K^+ is a quite large cation and the intensity of the electrostatic interaction with the negatively charged framework is lower than for other cations (e.g., Na^+) also present in zeolites of natural origin. According to the element percentages given in Table **2**, obtained by the natural clinoptilolite EDS analysis, the ratio between empty cationic sites and cationic sites occupied by charge carriers (K^+ cations) is given by: (at.%Ca+at.%Mg+2·at.%Fe)/(at.%K^+)=1.4. Therefore, there are approximately one and half empty sites for the hopping of each hydrated K^+ cation (see Scheme **1**).

The percentage of clinoptilolite crystalline phase (the only ionic conductive phase in the natural zeolite sample) was established by XRD and it resulted 40% by weight; the other crystalline phases were: stilbite (25%), cristobalite (22.3%), and anorthite (12.5%). Since zeolites of natural origin contain also solid phases that are not electrically conductive, in order to have a percolation network as extended as possible, they must be highly consolidated. Therefore, the high consolidation of geomorphic clinoptilolite is useful to achieve superior mechanical performance and the highest electrical conductivity. The average crystallite size was established by applying the Scherrer equation to the intensive (020) clinoptilolite peak (see Table **4**) and the achieved result (33.3nm) confirmed the value of thickness found by SEM investigation.

Table 2: Atomic Percentages of Different Elements in Natural Clinoptilolite as Determined by EDS

	Si	Al	O	K	Ca	Mg	Fe
%	23.38	4.27	69.01	1.55	1.03	0.34	0.41

Table 3: Absorbance Values used for the Spectroscopic (FT-IR) Determination of Si/Al

Bond type	Vibration type	Wavenumber (cm^{-1})	Transmittance (%)	Absorbance
Si-O-Al	Bending	670	90.25	0.0445
Si-O	Symmetric stretching	1018	68.67	0.163
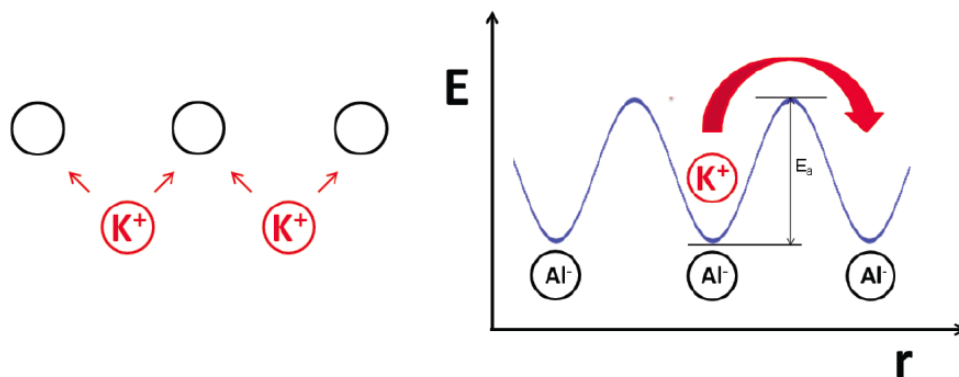
Scheme 1: Hopping possibilities for the hydrated K^+ cations (KOH$_2^+$) and relative energy barrier due to electrostatic repulsions with other cations.

Table 4:   Values used for the Lamellar Crystal Thickness Calculation by the Scherrer Equation (d=Kλ/βsinθ) [21]

Plane	2θ (°)	λ (Å)	K	β (rad)	d (nm)
(020)	9.8316	1.5406	0.94	0.25	33.3

The external zeolite sites for the physical adsorption of water molecules (surface hydrophilic sites) have a double nature: cations (Me^+) and silanol groups (Si-OH, Si-OH-Al). The presence of silanol groups can be proved by comparing shape and intensity of the three bands in the OH stretching region of the FT-IR spectrum of natural clinoptilolite (see Figure **2**) before and after a thermal drying treatment (1h at 150°C) (the infrared absorption bands are located at $3610cm^{-1}$, $3420cm^{-1}$, and $3256cm^{-1}$). Since only one of the OH stretching absorption band significantly reduces its intensity as a consequence of the thermal treatment (the absorption band of the water OH stretching group located at $3420cm^{-1}$), while the other two bands remain practically unchanged, silanol groups should be present in the sample. In fact, the concentration of these silanol groups on the sample surface is not depending on the thermal treatment undergone by the sample. Water adsorption on the external silanol groups does not contribute to the electrical conduction of clinoptilolite-based material, on the contrary, the presence of these groups reduces the sensitivity of the conductivity sensor to humidity because it reduces the number of water molecules detectable by an electrical measurement.

When a flat zeolite slab with silver painted electrodes (placed on the surface) is exposed to vapour of pure liquid water, its electrical conductivity grows according to the graph shown in Figure **3a**. Since water sorption takes place at high water vapour concentration (100% humidity), different sorption mechanisms (physical adsorption on the external crystal surface and external inter-crystalline mesoporosity, etc.) should be simultaneously involved during the process and the sorption follows a power law (see Figure **3a**), which is not one of the usual physical laws governing the adsorption phenomenon.

During desorption of water in air at 1atm and 20°C, the current intensity decreased up to reach a constant value (see Figure **3b**), which depended on the amount of residual hydrated cations.
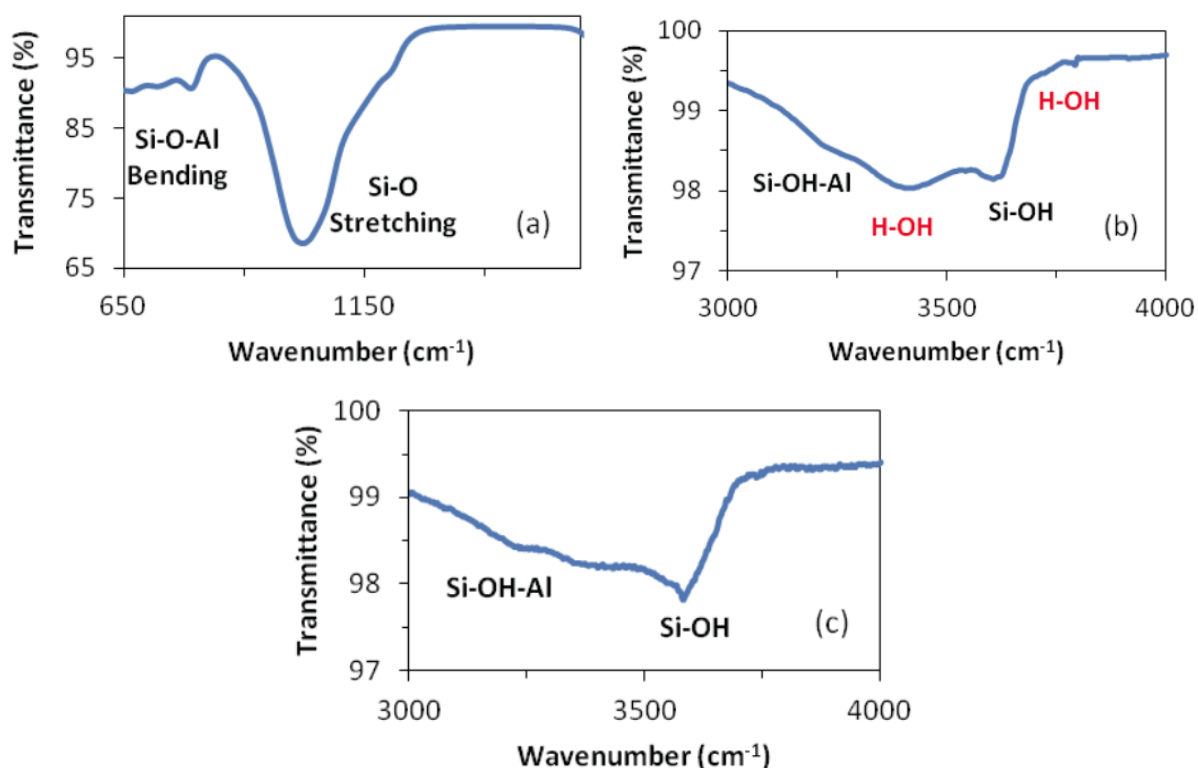

Figure 2: Resonances in the clinoptilolite FT-IR spectrum used for the Si/Al ratio calculation (**a**), and resonance attributed to the water adsorbed on the sample surface before (**b**) and after (**c**) the termal treatment (1h at 150°C).
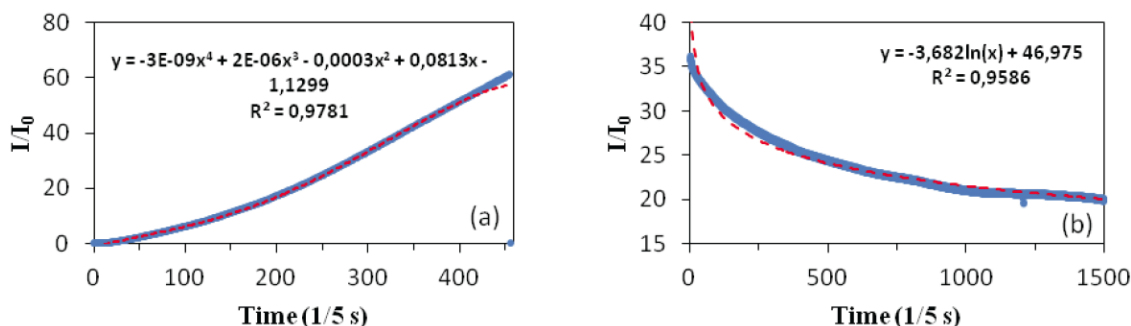
Figure 3: Behaviour of the clinoptilolite electrical conductivity during water vapour sorption (sensor exposed to the vapour of pure liquid water) (**a**) and behaviour of the clinoptilolite electrical conductivity during water vapour desorption in air (**b**).

Such material capability to change its electrical conductivity as a consequence of the water vapour exposition proved the possibility to technologically exploit these materials in fabricating humidity sensors that have shown to be fast-responding, reversible, and quite sensitive, and because of these characteristics this device might be used to detect the exhalation step of the human breathing, thus allowing to calculate the respiratory rate.

When the dynamic equilibrium between water in the vapor phase and water adsorbed on the clinoptilolite surface was modified (under isothermal conditions), a really prompt variation in the material conductivity resulted because of a change in the fraction of surface hydrated cations $(\alpha = [MeOH_2^+]/([Me^+]+[MeOH_2^+]))$, that depends on the environmental humidity concentration, $[H_2O]$, according to the following expression:

$$\alpha = \frac{[H_2O]}{\dfrac{1}{K_{eq}}+[H_2O]} \tag{1}$$

where K_{eq} is the equilibrium constant of the cation hydration reaction at room temperature:

$$Me^+ + H_2O \xleftrightarrow{\;K_{eq}\;} MeOH_2^+ \tag{2}$$

The relative current intensity at equilibrium is directly proportional to α and therefore it depends on the environmental humidity according to Eq. (1). Such a modification of the environmental humidity can be produced, for example, by breathing close to the clinoptilolite sample surface. This prompt variation of electrical conductivity was a consequence of the direct cation-water interaction. As visible in Figure **4a**, the clinoptilolite surface conductivity (observed as an increase in the sinusoidal current intensity) grows during each exhalation stage, but the material conductivity rapidly recovers the starting value at the

end of the exhalation (i.e., during the inhalation step). Therefore, this material can be used to fabricate quick-responding sensors to monitor the human breathing (exhalation) and measure its rate. Obviously, surface water adsorption/desorption kinetics regulates the behavior of this type of humidity sensor, in fact each breathing step in Figure **4b** consists of successive water adsorption and desorption processes.

An example of breathing pattern, including three breathing events, obtained by the voltage-drop technique, is shown in Figure **4b**. According to this breathing pattern, the surface resistivity was quickly modified in presence of the exhaled water vapor, and the voltage decreased of ca. 100mV. As visible, water adsorption was a very fast process that the datalogging system was able to record and followed a linear temporal behavior, differently desorption was a little slower and followed an exponential behavior. The comparison between the two breath patterns shown in Figure **4** evidences as the voltage-drop technique allows a very accurate visualization of the progressive hydration of the clinoptilolite sample surface, while information between the beginning and the end of hydration are completely lost in the case of current intensity measurement technique. Finally, according to the achieved graphical results, breath monitoring by the voltage-drop technique seems much more accurate than monitoring by the effective current intensity reading and therefore this technique can be more conveniently used to visualize the breathing profile in spirometry.

Depending on the presence or less of coordinated water molecules (see Figure **5**), the K^+ cation can move or not under an applied sinusoidal field and therefore the water adsorption causes a change in the material transport characteristics, that is detected as a charge flow (i.e., electric current intensity increase). It must be pointed out that the strong ability of zeolites to
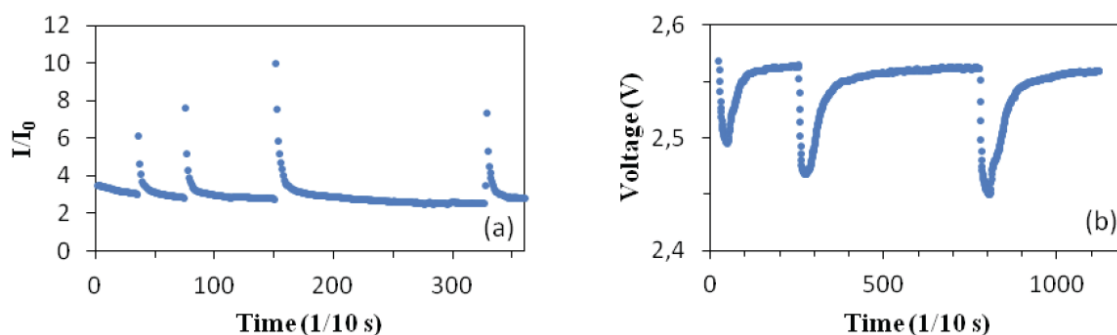
Figure 4: Sequence of four couples of water adsorption and desorption processes taking place in the natural clinoptilolite sample surface exposed to human breathing (**a**), and human breathing pattern obtained by the voltage drop technique (**b**).
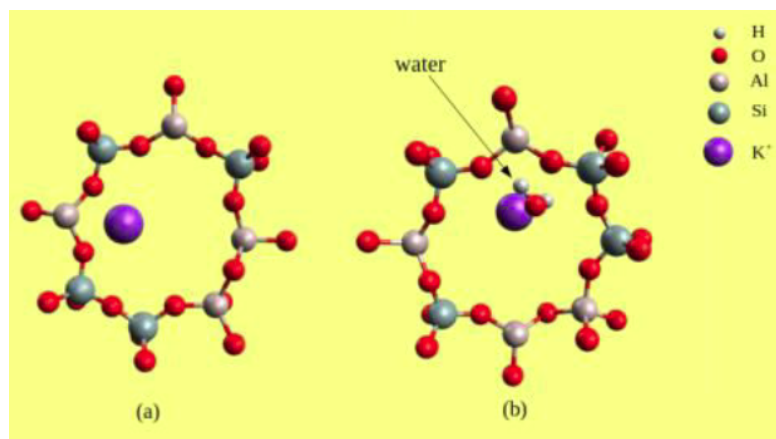

Figure 5: Depending on the hydration condition: (**a**) dry, and (**b**) hydrated, the K^+ cation can or not be a charge carrier.

physically adsorb polar and polarizable molecules on their external surface (independently from the size) and on their external/internal surface (in the case of very small molecules, like water) is a consequence of the presence of an electrostatic field near the surface. Such surface electrostatic field origins from the unbalanced electric fields of extra-framework cations and framework nucleophilic areas. In fact, while the electric fields generated by the positive and negative charges on the surface of an ionic solid are perfectly balanced because of the symmetric local organization of cations and anions. This symmetric charge distribution is lost in zeolite crystals because the negative charges in the framework are spread on a large area centered on the aluminium atom, which is located below the cation. This unbalanced electric field acts on the total dipole-moment of a molecule (e.g., H_2O) by long-range cation-dipole interactions. In particular, this special shape of the electric field does not allow simply a reorientation of the molecule total dipole moment, but it determines the translation of this molecule toward the solid surface. When molecules are as small as water, they can even penetrate the zeolite lattice and be stored inside the zeolite, near the internal cations. Differently, large molecules remain adsorbed on cations of the external surface. Molecular adsorption determines a decrease of the cation charge density because the positive charge results distributed on a larger volume made by the cation-molecule complex, and therefore a weakening of the electrostatic interaction with the nucleophilic area of the framework follows. Then, in order to maximize non-bonding interactions (i.e., Van der Waals bridges) with oxygen atoms on the framework surface, the molecule should move at cation-framework interface, thus allowing cation mobility under an applied electric bias and this significant mobility increase is promptly revealed as an increase of the surface electrical conductivity, which causes voltage-drop or effective current intensity increase.

4. CONCLUSION

The achieved results can be summarized as follows:

-   A mechanically robust zeolite-based sensing devices has been fabricated by using geomorphic clinoptilolite of natural origin.

- Zeolites are solid-state ionic conductors that can be used to fabricate water vapour sensors to be placed, for example, inside a standard oxygen mask to monitor the ventilation activity, they only requires to be combined with a simple electronic circuitry that displays and records the patients continuous respiratory rate by measuring the effective current intensity increase on the sensor surface or the voltage-drop at the sensor electrodes.

- The voltage-drop method for the exhalation stage detection has shown to be very accurate and capable to provide a very high resolution.

- These inexpensive sensing devices can be industrially exploited as breath rate monitor and/or personal spirometer in medicine (general anaesthesia, etc.) and sport fields.

REFERENCES

[1] Derakhshankhah H, Jafari S, Sarvari S, *et al.* Biomedical applications of zeolitic nanoparticles, with an emphasis on medical interventions. Int J Nanomed 2020; 15: 363-386.
https://doi.org/10.2147/IJN.S234573

[2] Joughehdoust S, Manafi S. Application of zeolite in biomedical engineering: a review, in Proc. of the Iran International Zeolite Conference (IIZC'08). April 29 - May1, 2008; Theran – Iran.

[3] Ghobarkar H, Schäf O, Guth U. Zeolites – from kitchen to space. Prog Solid St Chem 1999; 27: 29-73.
https://doi.org/10.1016/S0079-6786(00)00002-9

[4] Wernert V, Scäf O, Ghobarkar H, Denoyel R. Adsorption properties of zeolites for artificial kidney applications. Microporous Mesoporous Mater 2005; 83: 101-113.
https://doi.org/10.1016/j.micromeso.2005.03.018

[5] Hovhannisyan V, Dong C-Y, Chen SJ. Photodynamic dye adsorption and release performance of natural zeolite. Sci Rep 2017; 7: 45503.
https://doi.org/10.1038/srep45503

[6] Mgbemere HE, Ekpe IC, Lawal GI. Zeolite synthesis, characterization and application areas: a review. Int J Sci Environ Technol 2017; 6(10): 45-59.

[7] Li Y, Li H, Xiao L, *et al.* Hemostatic efficiency and wound healing properties of natural zeolite granules in a lethal rabbit model of complex groin injury. Materials 2012; 5: 2586-2596.
https://doi.org/10.3390/ma5122586

[8] Ninan N, Grohens Y, Elain A, Kalarikkal N, Thomas S. Synthesis and characterization of gelatine/zeolite porous scaffold. Eur Polym J 2013; 49(9): 2433-2445.
https://doi.org/10.1016/j.eurpolymj.2013.02.014

[9] Concepciòn-Rosabal B, Rodriguez-Fuentes G, Simòn-Carballo R. Development and featuring of the zeolitic active principle FZ: A glucose adsorbent. Zeolites 1997; 19: 47-50.
https://doi.org/10.1016/S0144-2449(97)00022-5

[10] Freeman DC, Stamires DN. Electrical conductivity of synthetic crystalline zeolites. J Chem Phys 1961; 35: 799.
https://doi.org/10.1063/1.1701219

[11] Cretikos MA, Bellomo R, Hillman K, Chen J, Finfer S, Flabouris A. Respiratory rate: the neglected vital sign. Med J Aust 2008; 188(11): 657-659.
https://doi.org/10.5694/j.1326-5377.2008.tb01825.x

[12] Urbiztondo M, Pellejero I, Rodriguez A, Pina MP, Santamaria J. Zeolite-coated interdigital capacitors for humidity sensing. Sens Actuators B Chem 2011; 157: 450-459.
https://doi.org/10.1016/j.snb.2011.04.089

[13] Zou J, He H, Dong J, Long Y. A guest/host material of LiCl/H-STI (stilbite) zeolite assembly: preparation, characterization and humidity-sensitive properties. J Mater Chem 2004; 14: 2405-2411.
https://doi.org/10.1039/b316040h

[14] Niesters M, Mahajan R, Olofsen E, *et al.* Validation of a novel respiratory rate monitor based on exhaled humidity. Br J Anaesth 2012; 109(6): 981-9.
https://doi.org/10.1093/bja/aes275

[15] Carotenuto G, Camerlingo C. Kinetic investigation of water physisorption on natural clinoptilolite at room temperature. Microporous Mesoporous Mater 2020; 302: 110238.
https://doi.org/10.1016/j.micromeso.2020.110238

[16] Lin CCH, Dambrowitz KA, Kuznicki SM, Evolving applications of zeolite molecular sieves. Can J Chem Eng 2012; 90: 207-216.
https://doi.org/10.1002/cjce.20667

[17] Alsawalha M, Overview of current and future perspectives of Saudi Arabian natural clinoptilolite zeolite: a case review. J Chem 2019; 3153471.
https://doi.org/10.1155/2019/3153471

[18] Carotenuto G. A new method to detect zeolite breath sensor response based on low-power square-wave sources. Eur J Eng Res Sci 2019; 48: 152-154.
https://doi.org/10.24018/ejers.2019.4.10.1594

[19] Sprynskyy M, Golembiewski R, Trykowski G, Buszewski B. Heterogeneity and hierarchy of clinoptilolite porosity. J Phys Chem Solids 2010; 71: 1269-1277.
https://doi.org/10.1016/j.jpcs.2010.05.006

[20] Jakobsson S. Determination of Si/Al ratios in semicrystalline aluminosilicate by FT-IR spectroscopy. Appl Spectrosc 2002; 56(6): 797-799.
https://doi.org/10.1366/000370202760077559

[21] Burton AW, Ong K, Rea T, Chan IY. On the estimation of average cristallite size of zeolites from the Scherrer equation: A critical evaluation of its application to zeolites with one-dimensional pore systems. Microporous Mesoporous Mater 2009; 117: 75-90.
https://doi.org/10.1016/j.micromeso.2008.06.010