Zeolite-Based Fast-Responding Sensors for Respiratory Rate Monitoring [†]

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Abstract: Wearable electrical sensors based on zeolites can be used for breath monitoring. The high silicon content of clinoptilolite makes this type of zeolite very adequate for fabricating sensitive water sensors. In addition to sensitivity, response fastness also represents a sensor characteristic of fundamental importance for breath monitoring. Here, the response fastness of a clinoptilolite-based water sensor has been evaluated by measuring the current intensity behavior upon exposition to a constant humidity atmosphere (75%). In particular, the clinoptilolite surface has been biased with a sinusoidal signal (20 V_{PP}, 5 kHz), and the true-RMS current intensity value has been recorded during exposition to the constant humidity atmosphere. Since current intensity is proportional to the adsorbed water concentration (only hydrated cations are charge carriers) a kinetic analysis has been possible. The clinoptilolite dehydration kinetics in a dry atmosphere have been evaluated too. According to this kinetic analysis, water adsorption is described by a Lagergren pseudo-first-order model with a rate constant of $(58.6 \pm 0.9) \cdot 10^{-4}$ min^{-1}, while desorption in dry air follows a first-order kinetic model with a specific rate of $(202.7 \pm 0.3) \cdot 10^{-4}$ min^{-1} at 25 °C.

Keywords: zeolites; natural clinoptilolite; water sensor; breath monitoring; adsorption kinetics

1. Introduction

The respiratory rate is related to a variety of physical responses, like: activity rate, stress, emotional activity, and many medical conditions [1]. Therefore, real-time monitoring of human breath can provide clinically relevant information [2]. In a clinical setting, the respiratory rate is determined by airflow monitoring (volume of inhaled/exhaled air per time unit). When wearability is required, other equivalent approaches can be used [3]. The measurement of the ribcage expansion/contraction, instead of airflow through the mouth, has been the first wearable solution to be adopted [4,5]. Although this method is effective and provides a fair amount of tidal breathing volume information, it is susceptible to movement noise, and requires wearing a special device to measure respiration. To meet the critical requirements of cost-effective wearable breath sensors, researchers developed novel types of sensors able to detect surrogate airflow signals (that is, some physical change taking place during breathing), such as humidity sensors [6,7], optical sensors [8], sound sensors [9], and thermal sensors [10,11]. Humidity sensors based on zeolites could represent a convenient choice, since devices based on these low-cost, nontoxic, biocompatible, and mechanically/thermally robust materials show very high sensitivity to water [12,13]. In particular, natural clinoptilolite is a high siliceous zeolite (Si/Al higher than 5) able to experience relevant conductivity changes by exposure to humidity, and consequently highly sensitive water sensors can

be fabricated by using this type of zeolite. Response fastness is another important aspect for sensors devoted to breath monitoring, because this property is required to achieve breathing patterns of good resolution, that contain reliable physiological information necessary to safely evaluate health condition.

The mechanism of humidity detection in zeolite sensor is based on the change of ionic conduction with the humidity level [13]. In particular, owing to the presence of extra-framework cations, electrical transport at the surface of a clinoptilolite sample depends on the environmental humidity [13]. In fact, at room temperature, the cation mobility is very low in a dry atmosphere, because of the strong electrostatic interaction between cation and the framework nucleophilic area, while it becomes much higher after that one water molecule has joined the cationic site. Thus, water adsorption modifies the charge carrier density (concentration of mobile cations), which reflects in a change of the intensity of current moving at the sample surface.

Here, the temporal evolution of a sinusoidal current signal (5 kHz), moving in a sample of natural clinoptilolite, during the water adsorption/desorption process, has been recorded and mathematically analyzed to estimate the kinetics of water adsorption/desorption. Adsorption was performed in a constant moisture environment (generated by using the saturation salt method [14]), while desorption was done in a dry atmosphere (made by activated silica gel). To exclude slow mass-transport through the zeolite microporosity, the investigation of this adsorption–conduction behavior, involving the extra-framework cations, has been limited to the sample surface by placing two coplanar electrical contacts on the clinoptilolite slab surface. Kinetic information on the molecular adsorption/desorption process are relevant for evaluating the performance of clinoptilolite as breath sensor respect to the responsivity and fastness properties.

2. Materials and Methods

Natural clinoptilolite (T.I.P. Germany) was used for this study in the as received form. In particular, small slabs were obtained by cutting the raw stone with a diamond saw.

The temporal evolution of the hydrated cation concentration was obtained by measuring the intensity of the electric current flowing on the sample surface biased by an a.c. voltage of 20 V_{PP} and 5 kHz during the process of water adsorption/desorption. A two contact method was used (electrodes were printed on the sample surface using silver paint) and the sample was exposed to a constant humidity atmosphere (75%) and dry air to monitor the adsorption and desorption kinetics, respectively. A high frequency voltage signal (produced by a sinusoidal source of 40 W, GW-Instek SFG-1013) was required to avoid charge accumulation at sample/electrode interface during the tests. The true-RMS current intensity was measured by a handheld digital multimeter (Brymen 869s) and recorded by the dedicated software (Bs86x Data Logging System Ver. 6.0.0.3s, Brymen, Taiwan) at time interval of 60 s. All measurements were done at room temperature. During the experiment the biasing voltage value (20 V_{PP}) remained practically constant, although there was a variation of the current intensity moving in the sample surface. In such conditions, the current intensity can be considered as proportional to the carrier concentration, since all ionic carriers have a constant local velocity.

The crystalline phases present in the natural zeolite sample were identified by XRD (X'Pert PRO, PANalytical). Si/Al ratio and type of contained ions were determined by SEM/EDS analysis (FEI Quanta 200 FEG microscope).

3. Result and Discussion

The commercial natural clinoptilolite sample was first characterized in order to establish the exact nature of the contained crystalline phases. Since zeolites are crystalline materials, X-ray diffraction (XRD) can be used to identify the solid phases present in the sample. As visible in Figure 1, the XRD diffractogram contains the diffraction patterns of clinoptilolite, anortite, and stilbite. In particular, the most intensive characteristic peaks of clinoptilolite are visible at 9.9446°, 22.4026°, 30.0076°, and 31.9576° [15]. The main peaks of anortite are visible at 21.9089°, 27.7716°, and 28.0837°, while stilbite has one main peak at 19.0616°.
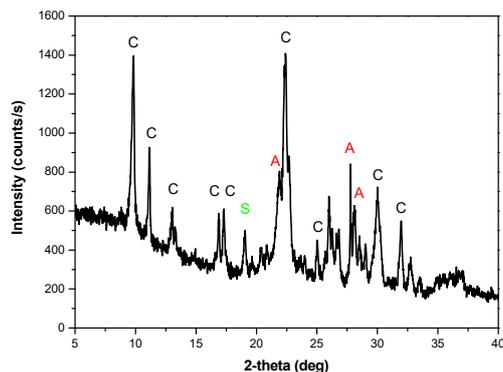
Figure 1. X-ray diffractogram of the studied natural clinoptilolite sample.

Figure 2 shows the SEM-micrograph of the natural clinoptilolite sample surface and the related EDS-spectrum. The zeolite has a compact structure, free from defects and macro/meso-porosity. Both the type of contained extra-framework cations and their approximate abundance were obtained by EDS analysis (see table in Figure 2b). According to this EDS analysis, the Si/Al ratio was 5.3.
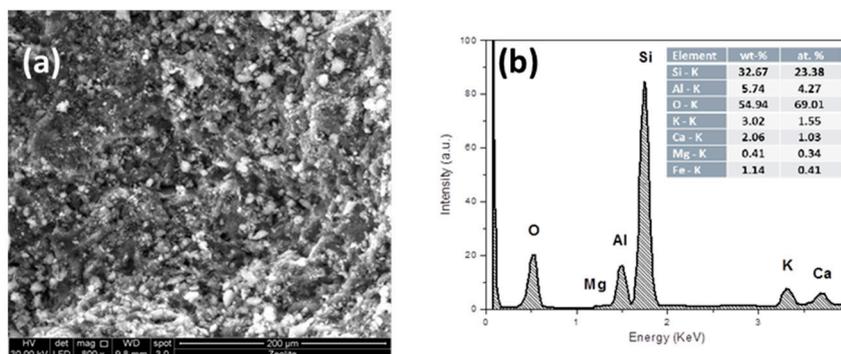

Figure 2. SEM-micrograph (**a**) and EDS spectrum (**b**) of the natural clinoptilolite sample.

The current intensity at sample surface, and therefore the carrier concentration, was promptly affected by exposition to humidity, thus confirming the role of cations in the water adsorption mechanism. In addition, a linear increase of the hydrated cation concentration was found (see Figure 3) by measuring the current intensity relative variation, during hydration of natural clinoptilolite exposed to constant moisture (75%).
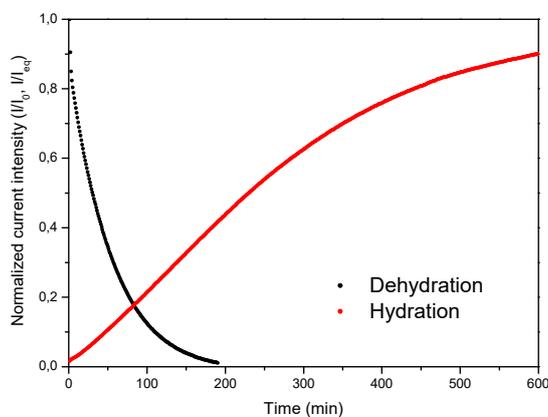

Figure 3. Temporal evolution of the normalized current intensity, during hydration and dehydration.

The electrical method allowed to directly investigate the kinetics of the water-cationic site interaction. Since the adsorbate fraction (f), that is, the ratio between the adsorbate concentration at t time and equilibrium, $f = Q_t/Q_{eq}$, is coincident with the corresponding current intensity ratio, I_t/I_{eq},

electrical data were used to establish the theoretical model of adsorption and therefore the kinetic constant, k. As visible in the graph shown in Figure 4a, the adsorption followed the well-known pseudo-first-order reversible model of Lagergren [16], that can be expressed by using the following linear form:

$$Log(1 - I_t/I_{eq}) = Log(1 - Q_t/Q_{eq}) = -(k/2.303) \cdot t \tag{1}$$

where k is the rate constant of pseudo-first-order reversible adsorption (min^{-1}). In fact, a plot of $Log(1 - I_t/I_{eq})$ against t has a linear behavior, the R-value (0.99973) is close to unit, thus indicating the suitability of this model, and k can be determined from the slope. In particular, the slope was 19.1×10^{-4}, and, because the water concentration was 0.75, it resulted $k = (58.6 \pm 0.9) \cdot 10^{-4}$ min^{-1}.
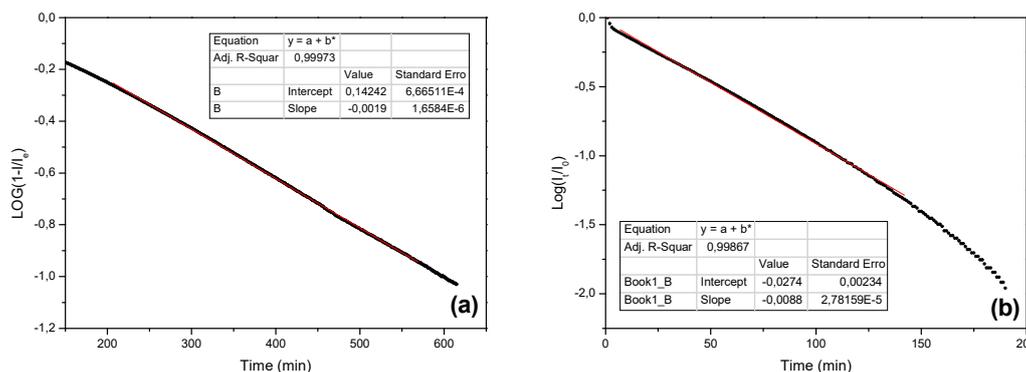

Figure 4. Fitting of the current intensity data by the pseudo-first-order model of Lagergren (**a**) and behavior of the relative current intensity logarithm during water desorption from a natural clinoptilolite sample (**b**).

Figure 4b shows the temporal behavior of the relative current intensity logarithm, which corresponds to the logarithm of residual adsorbate fraction, $f = I_t/I_0 = Q_t/Q_0$, during sample dehydration in dry air. As visible, this quantity follows a linear behavior, indicating that the dehydration kinetics was described by a first-order kinetic model (the R-value is 0.99867, thus very close to unity, which indicates the feasibility of the first-order kinetic model). This model describes exactly the process inverse to that described by the adsorption model, thus confirming the model adopted for the adsorption. This model is typically observed in the release of gaseous molecules from a zeolitic material [17].

$$Log(Q_t/Q_0) = -(k'/2.303) \cdot t \tag{2}$$

The slope of the linear curve gives the specific rate for dehydration in dry air and it is: $(202.7 \pm 0.3) \cdot 10^{-4}$ min^{-1}. As visible, the rate constant of desorption is one order of magnitude higher than for adsorption, and therefore the reversible adsorption equilibrium constant has a very low value ($K_{eq} = k/k' = 0.29$).

When the dynamic equilibrium between water in the vapor phase and water adsorbed on clinoptilolite surface was perturbated (under isothermal conditions), a very prompt change in the material conduction was observed. Such a perturbation 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 5, the clinoptilolite surface conductivity (observed as an increase in the a.c. current intensity) grows during each exhalation stage, but the material conductivity rapidly recovers the starting value at the end of exhalation (i.e., during the inhalation step). Therefore, this material can be used to fabricate quick-responding sensors to monitor human breathing and measure its rate. Obviously, the above described water adsorption/desorption kinetics regulates the behavior of this type of humidity sensor, in fact, as shown in Figure 5, each breathing step consists of successive water adsorption and desorption reactions.
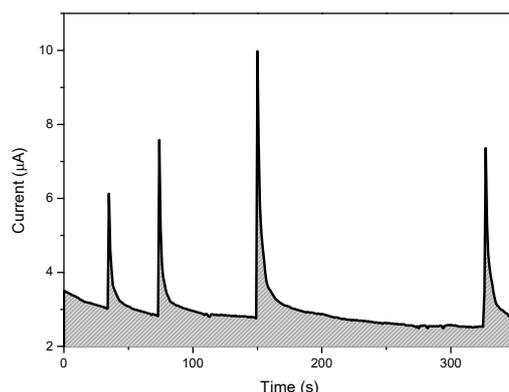
Figure 5. Sequence of four couples of water adsorption and desorption processes, taking place in the natural clinoptilolite sample surface exposed to human breathing.

4. Conclusions

Owing to the high sensitivity and fast response, water sensors based on high siliceous natural clinoptilolite (Si/Al = 5.3) could be used as wearable sensors for breath rate monitoring. The water adsorption/desorption kinetic analysis performed at room temperature on natural clinoptilolite by an electrical approach has shown an adsorption specific rate (k = $(58.6 \pm 0.9) \cdot 10^{-4}$ min^{-1}) adequate for monitoring human breathing. In particular, water adsorption in a 75% humidity environment follows a Lagergren kinetic model (pseudo-first-order), while water desorption in a dry atmosphere follows a first-order kinetics with a kinetic constant of $(202.7 \pm 0.3) \cdot 10^{-4}$ min^{-1}.

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