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Specific Electrical Conductivity of Natural Syrian and Armenian Zeolites

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The direct current (dc) conductivity of several natural Syrian and Armenian zeolitic samples is measured in order to understand the mechanism of electrical conductivity in these materials. The influence of the sample's water content on its electrical conductivity is studied in details. We find that with the increase of hydration time or, equivalently, the increase of water content in the sample, the electrical conductivity of the samples increases up to a definite moment at which the increase stops. This moment is characteristic of each sample and it corresponds to the saturation state which means the state where the hydration process is finished and that the sample has reached its equilibrium state corresponding to an air-dried sample. We compare our results with available experimental data of relatively other materials and find that they agree in general.

Introduction

The measurement of the specific electrical conductivity σ of zeolites is one of the most attractive procedures to determine their properties [1–10]. Usually, the measurement of σ of zeolitic samples takes place at the alternative current (ac) condition (variable electrical field) in order to avoid various effects such as polarization, relaxation processes, electrolyze, etc [1–8]. In this case, however, σ is highly dependent on the applied frequency of the electrical field. Therefore, it is recommended that one measures σ within a wide range of frequencies in order to have an idea, sufficiently correct, about the mechanism of electrical conductivity in the zeolites [2]. Moreover, the measurement of σ at constant electrical field conditions (direct current (dc) conditions) somehow gives an overestimate. The results of the measurements, obtained using these two methods, could be integrated in order to give a real picture of the electrical conductivity [3–7].

In addition to the above mentioned properties, it is well known that zeolites have a large forbidden energy gap ($\sim 7\text{eV}$) [8], and that their electrical conductivity, in value, is near to that of bad dielectrics. On the other hand, the characteristic behavior of the electrical conductivity of dielectrics is such that when applying a constant electrical field on a dielectric sample, the intensity of the current, passed through the sample, decreases with time [11–13]. In fact, at the start, bias current with quickly decreasing intensity passes through the circuit, then, this current disappears at a time equal to the order of the RC system (generator-sample) constant time, which is very small (less than 1 s). However, the current can continue its decrease for some minutes, voire some hours in cases of samples with big dimensions. The time required for current stabilization could be decreased by adjusting the dimensions of the sample.

The component of slow changing current is due to the redistribution of free charges in the volume of the dielectric. This component is known as the absorption current,

and it is caused by the absorption of free current carriers in the volume of the dielectric. Part of these carriers, during their movement, will meet defects-traps of crystalline lattice causing them to be trapped and stopped. With time, the traps could be filled by current carriers, then, the absorption current disappears. The rest of the current does not depend on time and it is due to the charge carriers which pass from one side of the sample to the other (i.e. from one electrode to another). Thus, the absorption current leads to the accumulation of current carriers in separate parts of the dielectric, for example in the destroyed parts of the crystalline lattice, or at the grain boundaries, or/and in other types of inhomogeneities. As a result of the space charge appearance, the distribution of the electrical field becomes inhomogeneous. The accumulation of space charge in the dielectric leads to an undesired phenomenon in that the charged capacitor does not discharge totally after wiring its plates (short circuit). This effect is characterized by the coefficient of absorption which is determined as the ratio of the residual to the initial voltage.

When measuring the specific electrical conductivity, the absorption current could be eliminated by applying temporarily a constant voltage on the sample electrodes. All what we mentioned of phenomena do happen in the zeolitic samples and the arguments above do apply. Thus, the measurement of the specific electrical conductivity of zeolites is completed, in fact, by measuring the current which passes through the samples, i.e. the steady leakage current [11].

Our work deals with the measurement of the specific electrical conductivity of natural Syrian and Armenian zeolites.

1. Experimental Set-Up

In order to measure the dc conductivity σ , a universal voltmeter V 7-16 is used with an input resistance equal to $10\text{ M}\Omega$ (for dc), in addition to a nano-voltmeter P-341 having an input resistance of $100\ \Omega$ approximately and minimal scaling of 0.005 nA (for dc). Since the input resistance of the voltmeter is less than the resistance of the sample itself (or near to it), the voltmeter is not connected to the sample directly. As usually done, in the case of samples with low resistance, the voltmeter should be connected in parallel to the sample and to the Amber meter simultaneously in order to avoid current pass through the voltmeter. The mentioned scheme is well described in the literature. In fact, the voltmeter is connected to one side of the sample while the other side is connected to the Amber meter.

2. Sample Preparation

In this work, the investigated samples have been prepared from grounded Syrian (S and M) and Armenian (A) natural zeolites. The Armenian zeolite, denoted by A11, contains up to 85% of clinoptilolite with a ratio of Si/Al equal to 9.8 [14] and amorphous SiO_2 less than 3%. Around 50% of the Syrian zeolitic substance contains, mainly, the three types of zeolite (analcime, phillipsite and chabazite). Other contaminations in raw materials for Armenian natural zeolite are: feldspar — 5%, quartz — 5%, mica — 2%, clays — 3%, whereas these values are quite different in the natural Syrian zeolite where the availability of calcite, quartz, clays and amorphous phase is proven in most of the samples. The quantity of each of the mentioned minerals depends on the location of the site from which the sample was taken along the borehole. These results were obtained by chemical and thermo-gravimetric analysis. According to this analysis and measurements, the endothermic effect of dehydration is observed at the temperatures between 70° and 300°C with simultaneous mass loss of up to 8.2% [14].

The chemical composition of the studied samples is given in Table 1. Zeolite powder was pressed into pellets at pressure of 200 kg/cm^2 . The pellet was mechanically cut out into rectangular samples with area of approximately 30 mm^2 and thickness of 2–3 mm. On both sides of the sample surfaces, silver contacts were made. Then, the samples were annealed at temperature 120°C for two hours, followed by thermal treatment at

220°C for two extra hours in the surrounding environment. This processing makes it possible to obtain reliable silver contacts. Measurement was carried out in the air and at temperature 24°C at relative humidity of 50–55%. The sample was stored at normal atmospheric pressure and it contained, of its weight, about 11.2% water. The sample temperature was measured by germanium diode with accuracy of ± 0.2 K.

The chemical composition of the studied samples Table 1

L.I.	P ₂ O ₅	Cr ₂ O ₃	Mn ₂ O ₃	TiO ₂	MgO	Fe ₂ O ₃	CaO	K ₂ O	Na ₂ O	Al ₂ O ₃	SiO ₂	Sample
14.19	—	—	—	0.20	1.28	2.23	4.9	2.22	0.79	11.69	67.11	A11
12.3	0.44	0.03	0.2	1.60	12.21	11.68	8.77	1.01	1.22	10.48	39.51	2S14
14.10	0.46	0.03	0.17	1.48	11.09	10.41	11.01	0.89	0.93	9.98	38.69	4S14
15.16	0.52	0.03	0.17	1.60	9.74	10.65	11.92	1.08	0.99	10.15	37.64	6S14
16.52	0.52	0.03	0.15	1.37	8.55	8.97	14.95	0.84	0.75	9.80	37.14	8S14
10.98	0.41	0.04	0.22	1.64	14.17	13.20	6.73	1.02	1.13	10.42	39.95	10S14
10.46	0.49	0.03	0.20	1.84	9.99	12.02	8.24	1.13	1.50	11.65	40.76	12S14
10.71	0.47	0.03	0.18	1.75	10.65	11.75	8.95	1.13	1.66	10.97	40.17	M5
9.28	0.52	0.03	0.20	2.10	9.01	12.60	8.26	1.24	1.45	13.04	41.36	16S14
9.31	0.49	0.03	0.19	1.92	10.45	11.99	8.18	1.19	1.43	12.00	41.08	18S14
9.24	0.47	0.03	0.19	1.87	10.62	12.30	7.96	1.18	1.65	11.63	41.23	20s14

Measurements of electro physical parameters were carried out on pressed samples. The samples are made of Syrian and Armenian natural zeolite powder (with grain size of 50 Micron). It should be noted that, after switching the constant electric field, the current passing through the sample is established at a time interval which gets beyond several hours sometimes (especially for large samples). This means that, in these cases, relaxation processes are taking place. The main reason for such relaxations is the polarization of the sample which can be taken into account by a well known method [11–13].

We should mention here that during the period of storage, relative changes in the weight of the samples due to weather changes did not surpass 0.5 l. The absolute accuracy in the weight measurement was 0.05 mg; hence the accuracy of measurement for σ is about 5%.

3. Results and Discussion

After having carried out the thermal treatment according to the above mentioned methodology, the dc conductivity of dried air samples was measured at a temperature equal to 24°C using a constant electrical field of $1 \div 3$ V/cm. The weight of the sample was measured also with an absolute accuracy of ± 0.05 mg.

In order to study the influence of the sample’s water content on its electrical conductivity, all the studied samples were put in a closed container for 4–5 days at a saturated vapor pressure corresponding to a temperature equal to 24°C. This procedure allows the samples to reach their state of total saturation. After that, each one of the studied samples was put in a special cell and its dc electrical conductivity was measured dynamically as a function of time at open air conditions. Thus, we could acquire the dependence of the dc conductivity on the dehydration degree. The dehydration degree is determined as $d_h = (m_0 - m) \cdot 100\% / m_0$, where m_0 is the mass of the sample with maximal water content and m is the current mass of the same sample. Some of the obtained results are given in Table 2. In addition, we present in Figure 1 the dependence of dc conductivity of Armenian sample (A_{11}) on the dehydration period length. After dehydration, Syrian samples became unsuitable for measuring the dc conductivity since they conserved weakly their shape after the pressing. This is due, perhaps, to the inclusion of different phases in these samples

(especially quartz and different zeolitic types). These samples could be destroyed when they reached total saturation. Therefore, the electrical conductivity of the Syrian samples was measured at the hydration mode, starting from partially dehydrated state up to totally dehydrated one. Therefore, the results corresponding to the state of total saturation are not given in Table 2 (see 2nd column). We think that these data can be completec

technology.

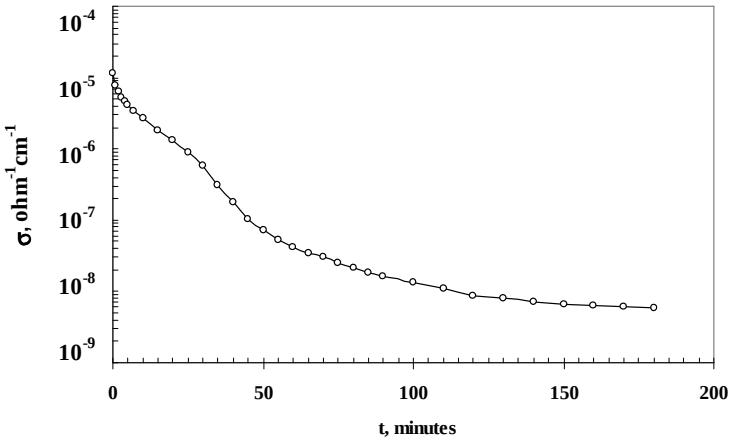


Figure 1. The hydration time variation of the specific conductivity of natural Armenian zeolite (clinoptilolite) at temperature 24C

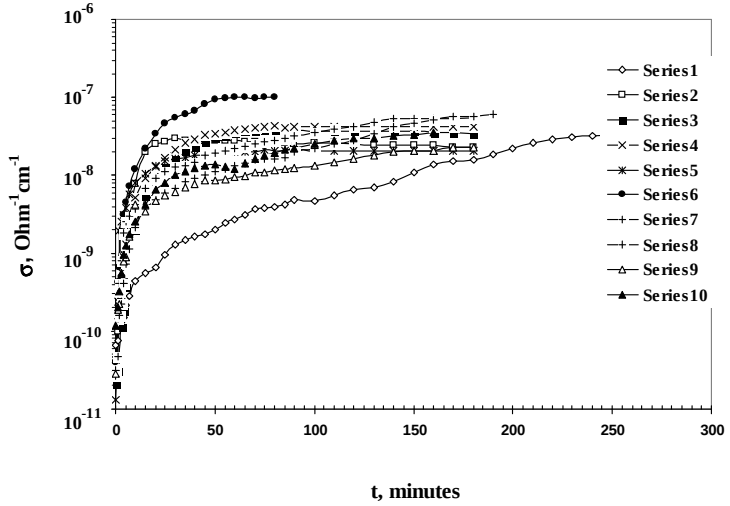


Figure 2. The hydration time variation of the specific conductivity of natural zeolitic samples at temperature 24°C. 1-A11; 2-M5; 3-2S14; 4-4S14; 5-6S14; 6-8S14; 7-10S14; 8-12S14; 9-16S14; 10-20S14

It should be noted also that the dehydration degree (c.f. the 1st row in Table 2) is evaluated using for m_0 the value of the mass when the sample was at the state of total saturation. In contrast, the evaluation, in the other rows, was made using for m_0 the value at the partial dehydration state which corresponded to when the sample was thermally treated for two hours in open air conditions at temperature 220°C. It is seen from Figure 1 that the sample A_{11} reaches its equilibrium state

Table 2
Specific electrical conductivity at T=24°C for natural Armenian (A₁₁) and Syrian (M and S) zeolites corresponding to different degrees of dehydration d_h

Samples	σ (in $10^{-11} \Omega^{-1}\text{cm}^{-1}$) for corresponding degree of dehydration (in %)		
A ₁₁	1200000 for d _h = 0	677 for d _h = 9.22	1.5 for d _h = 14.8
A ₁₁	—	1220 at ambient air	6.58 for d _h = 5.73
M5	—	618 at ambient air	3.52 for d _h = 6.65
2S14	—	1190 at ambient air	2.07 for d _h = 5.32
4S14	—	1930 at ambient air	4.25 for d _h = 4.8
6S14	—	2210 at ambient air	1.31 for d _h = 6.4
8S14	—	4030 at ambient air	4.04 for d _h = 4.3
10S14	—	4290 at ambient air	2.68 for d _h = 6.16
12S14	—	2860 at ambient air	3.14 for d _h = 7.4
16S14	—	1480 at ambient air	2.84 for d _h = 5.52
20S14	—	1730 at ambient air	11.9 for d _h = 5.3

within three hours, and here the dc conductivity becomes independent of time. In this case, the sample passes from total saturation state to dried-air state as a result of water emigration from the sample to the surrounding air. In other words, we have a dehydration sample at that time. This situation is accompanied by σ , decrease from $1.2 \cdot 10^{-5} \Omega^{-1}\text{cm}^{-1}$ to $6.77 \cdot 10^{-9} \Omega^{-1}\text{cm}^{-1}$ in the case of Armenian samples. The measured values of dc electrical conductivity for all samples at some values of dehydration degree are presented in Table 2. It is characteristic of sample A₁₁ that the dependence of its conductivity on the water content in the mode of hydration differs from that of the hydration mode. This can be seen clearly by dividing the values of the dc conductivity, given in the 3rd column of Table 2, by the corresponding values in the last (4th) column in the same table to give the dc value of σ , the partially dehydrated state. In such a way, for Armenian samples, we find ($677/1.5 = 451$) and ($1220/6.58 = 185$) respectively. This behavior of conductivity at the mentioned two modes agrees well with the isothermal curves of sorption and desorption. For the Syrian samples, the following values were obtained (see Table 2, from top to bottom) 175; 575; 454; 1687; 998; 1600; 911; 521 and 145 respectively. The dependence of $\sigma(t)$ on the hydration time is illustrated in Figures 2–5. Figure 2 contains the data for all samples, whereas, for clarity and to make the comparison easier, the samples' data have been divided into groups and are presented in Figures 3–5.

It is seen from Figures 2–5 that with the increase of hydration time (i.e. with the increase of water content in the sample) the electrical conductivity of the samples increases until a definite moment when the increase stops. This moment is characteristic of each sample and it corresponds to the saturation state indicating that the hydration process has been finished and that the sample has reached its equilibrium state (air-dried sample). For some samples, this process goes relatively quickly (from 0.5 hour to 1 hour) while for others it goes more slowly. One can also notice additional stages on the curve of time dependence of electrical conductivity $\sigma(t)$. This is due, probably, to the inhomogeneous phase content of the corresponding samples.

Moreover, when comparing σ for natural Armenian and Syrian zeolitic samples one finds that during the process of establishing total hydration, the value of σ increases 2.5 times in magnitude for the Armenian samples, while for the Syrian samples, the same value triples its magnitude, and sometimes increases even more.

On the other hand, one can compute from Table 1, where the oxide contents of Armenian and Syrian samples is given, the molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ for these samples. When doing this, we find that this ratio is in the range ($3.17 \div 3.88$) for the Syrian

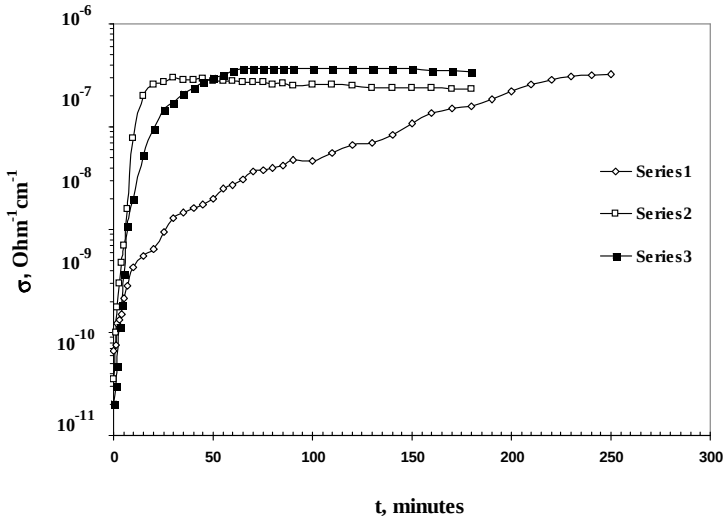


Figure 3. The hydration time variation of the Specific conductivity of natural zeolitic samples (1-A11; 2-M5; 3-2S14) at temperature 24°C.

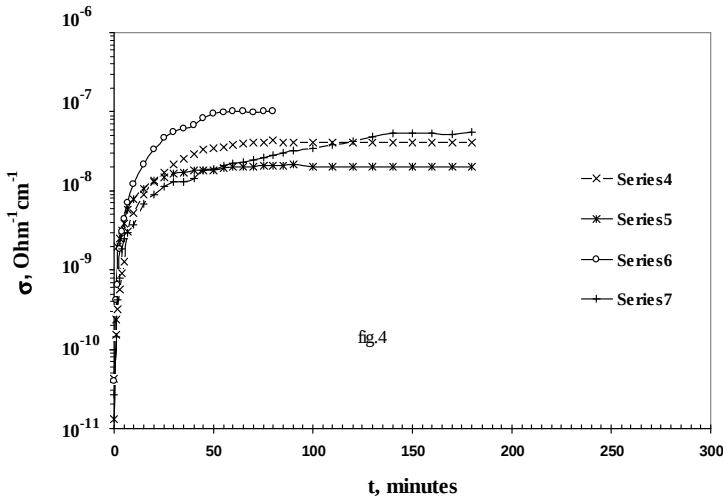


Figure 4. The hydration time variation of the Specific conductivity of natural Syrian zeolitic samples (4-4S14; 5-6S14; 6-8S14; 7-10S14) at temperature 24°C

samples, while its value, for Armenian zeolite, could change in the range (5.74 ÷ 5.91) [14]. It is known [2,9,10] that samples with smaller values of this ratio are more conductive and less stable. Whence, the higher values of electrical conductivity of Syrian samples could be explained. However, it should be mentioned that, at relatively low temperatures, the measured values of σ and the stability of zeolitic samples are determined by their cation contents [1,9].

The mechanism of conductivity in zeolitic samples has a jumpy character and the ions or protons play, in general, the role of current carriers [1,2,5–7]. The content and the structure of the zeolitic sample determine its sorbitizing properties, in relation to water vapors [2,9,10]. In this case, with the increase of water content, σ increases while the tilt of the curve of $\lg \sigma$ dependence on water concentration decreases. This

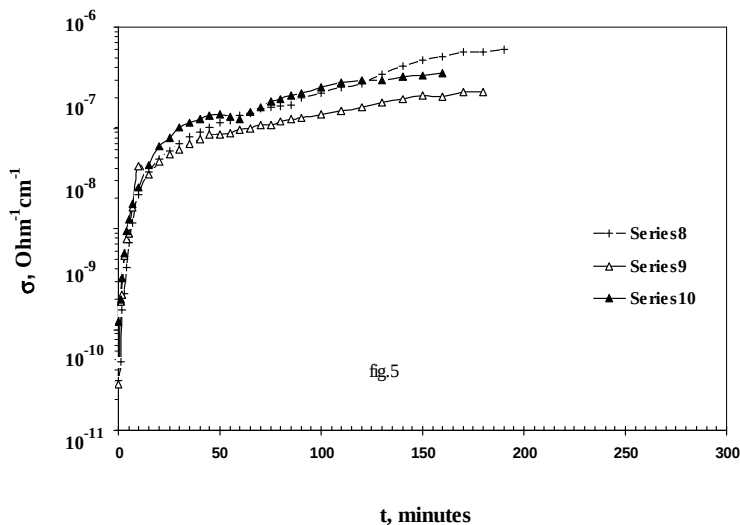


Figure 5. The hydration time variation of the specific conductivity of natural Syrian zeolitic samples (8-12S14; 9-16S14; 10-20S14) at temperature 24°C

means that the activation energy of conduction decreases also [2, 9, 10]. In our case, the availability of different tilts on the curve $\lg \sigma - t$ confirms this result.

Conclusions

One can conclude that the complete explanation of the observed phenomena requires measuring σ in wider ranges of temperature, hydration and studied samples. This can be achieved using different chemical and radiation methods [5–7, 14, 15]. These results should be accompanied as well by the results of other related physical measurements. We have to mention also that the measurement of surface conductivity in addition to the volume conductivity could help in understanding many phenomena especially the process of sorption which passes through the surface. At present, we are doing this kind of measurement and the preliminary results show that it is highly sensitive to the humidity and temperature in comparison with the volume conductivity.

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Удельная электрическая проводимость натуральных цеолитов из Армении (клиноптилолит) и Сирии

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В этой работе мы проводили измерения электрической проводимости (σ) натуральных цеолита Сирии и Армении в постоянном электрическом поле. Изучены влияния влажности на проводимость образцов. Для всех образцов проводились временные зависимости проводимости (в режиме гидратации) от частично обезвоженного состояния до воздушно-сухого состояния. Можно отметить следующие основные результаты: с ростом времени гидратации (т. е. с ростом содержания воды) наблюдается увеличение проводимости образцов, и через некоторое время она достигает насыщения, что означает конец процесса гидратации, образец переходит в равновесное состояние (воздушно-сухой образец).