

ELECTRICAL PARAMETERS OF ZEOLITE WITH DIFFERENT SILVER CONTENT

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The zeolite is actively used in various fields of medicine and biology as an active substance to fight bacteria and as an element of an electrical circuit. In the present paper these studies were carried out on the basis of natural clinoptilolite zeolite and its modification with silver. In this investigation the electrical parameters of zeolite with different silver content were studied. Two types of samples were studied: 1) after treatment in different AgNO₃ solution (samples N1 and N2); 2) after treatment of (N-1) and (N-2) in NaBH₄. The electrical conductivity of the samples was studied by changing the pressure in the chamber. It was found that the electrical conductivity depends on the concentration of silver and the pressure in the chamber. The study of these samples revealed some features. Due to the high content of silver ions in the zeolite, current stabilization is observed. The pressure in the chamber does not affect the current as the concentration of neutralized silver increases. This is due to the fact that the concentration of silver ions accumulates at the ends of the sample.

Keywords: zeolite, electrical conductivity of zeolite, silver content zeolite, dependence on silver concentration.

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1. INTRODUCTION

The state of the molecular system in the pores of the solid-state matrix is of significant interest both from the point of view of fundamental science and practice [1-2].

Zeolites are classic representatives of nanoporous materials. The value of zeolites is due to the openwork aluminum-silica framework common to these materials, of pores and cavities which forms a system of pores and cavities, the size of the entrance windows of which is large enough for molecules and ions of most organic and nonorganic compounds to penetrate into them. The framework of zeolites is similar to honeycombs and formed from the cores of silicon and aluminum anionites. Due to its structures, the framework has a negative charge, and this charge is compensated by water molecules and cations of alkaline and alkaline-earth metals weakly bound to it. The pores of zeolites of regular shape, connected to each other through 'windows', form a network of through channels inside the crystal. Therefore, zeolites can be considered as an object on which, in addition to the already well-known phenomena (adsorption, ion exchange phenomena), can investigate the pore emission of electrons, electron multiplication and gas discharge in the pores, dielectric and electrical properties, when the pores are saturated with various gases and liquids. On the basis of X-ray and spectral chemical analysis, the affiliation of the studied natural zeolite to high-silica zeolites of clinoptilolite type was established [3]. The crystal structure of clinoptilolite belongs to monoclinic syngony with parameters; $a = 17.74 \text{ \AA}$, $b = 17.9 \text{ \AA}$, $c = 7.4 \text{ \AA}$, spatial group C2/m, $\beta = 117^\circ$. The structure consists of alternating negatively charged aluminosilicon-oxygen tetrahedra AlO₄ and SiO₄, which connecting with each other by vertices, form pores-nanochannels of two types A and B with sizes 0.6·4 nm (A type) and 0.4·0.4 nm (B type). The contents of these channels are an out-of-frame subsystem: this is positive charge ions- cations of Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺, that

compensate for the negative charge of the framework, and also a large amount of coordination water molecules.

In microelectronics the conductivity of zeolites is usually associated with ionic conductivity [3-4]. The conduction current is carried out by the movement of mobile balancing ions in an anionic framework. Hydrated zeolites are also known as proton conductors [5]. Usually, as a rule, it is assumed that electronic conductivity is not realized in zeolites [6]. In addition, materials, such as zeolites have the ability to store energy when the external electric field is applied [7]. Special electrical properties of nanoporous of zeolite structures make zeolites candidate materials in microelectronics [8]. Zeolites are used as gas sensors [9], solar panels [10], functional fillers in composites [11], plasma light sources with low-energy consumption [12].

Thus, it can be seen, the zeolite is actively used as an element of an electrical circuit. However, until now no systematic study of zeolite, as an element of electrical circuit, has been carried out. This refers to the study of the frequency dependences of the dielectric permittivity and conductivity of natural zeolite and its modification. In this paper, these studies were carried out for natural clinoptilolite zeolite and its modification with silver. The zeolite modified with silver was chosen because it is actively used in various fields of medicine and biology as an active substance to fight bacteria [13] and because silver is one of most highly conductive substances. Therefore, we conducted studies to determine the effect of silver modification of clinoptilolite on its electrical properties.

2. MATERIALS

The zeolite used in the experiment as a dielectric matrix, was a natural zeolite (NZ) of the clinoptilolite type. Its structure is composed of alternating negatively charged aluminosilicate tetrahedral AlO₄ and SiO₄, which, when combined, form charged frameworks, in

the pores of which there are positive ions- cations to compensate for the negative charge of the framework. Mapping and the characteristic elemental composition of cations in the pores were studied by scanning electron spectroscopy (SEM) on the JEOL JSM 7600F device. The pores contained ions of Na, Ca, K, Mg. Clinoptilolite after ball mill processing turned into powder, consisting of crystallites with dimensions of 0.5 - 30µm.

Modification of clinoptilolite with silver was carried out in order to:

a. exchange sodium ions for silver ions in a solution of silver nitrate (AgNO₃) of various concentrations (0,02M and 0,1M), in order to obtain two types of zeolite powders with different content of silver ions in the pores;

b. process powders of both types in a solution of sodium borohydrate (NaBH₄) for remission of silver ions into neutral silver.

Thus, as a result of ion exchange in AgNO₃ solution of various concentrations (0,02M and 0,1M), zeolite powders with different silver content in the pores were obtained. For the chemical reduction of silver ions to neutral silver (Ag nanoparticles), solutions of sodium borohydrate (NaBH₄) 0.1M were prepared. Powders with ion-exchange silver were immersed in NaBH₄ solution for 40 seconds, then washed with distilled water and dried at 550°C.

As a result, the following samples were obtained for the study:

- (N-1) – the powder containing Ag⁺ ions after treatment in AgNO₃ solution 0,02M;

- (N-2) – the powder containing Ag⁺ ions after treatment in AgNO₃ solution 0,1M;
- (N-10) –the powder with neutral silver Ag after treatment of (N-1) in NaBH₄ solution;
- (N-20) – the powder with neutral Ag after treatment of (N-2) in NaBO₄ solution.

To carry out the electrical measurements at constant voltage, the powder was placed in a cassette, where it was clamped between two electrodes. The cassette was placed in the chamber equipped with electrical inputs and outputs for pumping gas out of chamber. The pressure in the chamber was recorded by a pressure gauge. The constant stabilized voltage was in the range of 40 – 1000V. The current was recorded in the range of 10⁻⁸– 10⁻³A, the pressure varied from atmospheric (p_{atm}) to 10⁻²Torr.

3. EXPERIMENTS

The experiment consisted from the following.

At constant voltage the following parameters were measured:

- a) the dynamics of the current I(t) after switching on the constant voltage U= 100V at constant pressure p_{atm} ;
- b) the dependence of the current on the remaining pressure I_p in the range of 760 – 10⁻¹Torr.

The results obtained at constant voltage are presented in Table1, where Ag (%) is the percentage of silver in the powder, $I_0(A)$ - primary current, t is the time, R - is the resistance, $I_p(A)$ (0,1Torr) is the current at a pressure of 0,1Torr;

Table 1.

Samples	Ag (%)	I_0 (A)	t (min)	R (MΩ)	I_p (A) (0,1Torr)
after treatment in different AgNO ₃ solution					
(N-1) (Ag ⁺ , AgNO ₃ , 0,02M)	3,0	$8,5 \cdot 10^{-5}$	25	2,2	$\leq 10^{-7}$
(N-2) (Ag ⁺ , AgNO ₃ , 0,1M)	10,2	$12 \cdot 10^{-5}$	∞	0,8	$7 \cdot 10^{-7}$
after treatment of (N-1) and (N-2) in NaBH ₄					
(N-10) (Ag, treatment (N-1) in NaBH ₄)	6.5	$4 \cdot 10^{-5}$	20	4.8	$\leq 10^{-7}$
(N-20) (Ag, treatment (N-2) in NaBH ₄)	13.8	$17 \cdot 10^{-5}$	∞	0.57	$3 \cdot 10^{-4}$

It was assumed that since the concentration of the solution silver nitrate (AgNO₃) for N-2 is 5 times higher than the solution for N-1, then, accordingly, the current in the N-2 sample will be 5 times higher than in the N-1 sample. But as can be seen from the table, the currents differ only 1,4 times.

However, the dynamics of currents after switching on a constant voltage of 100V differs significantly: in the sample (N-2) the current is stable, and in the sample (N-1) the current decreases with time. This current drop is estimated by the amount of time t , during which the current is reduced by half. For sample (N-1) this time is 25 min., for sample (N-2) $t = \infty$. The resistance (R) of the samples was defined as the ratio of the applied voltage to the stable current for the sample (N-2) and the ratio of the voltage to the weekly

varying current over time t for the sample (N-1). They differ by 3 times.

The current in the sample N-1 decreased with decreasing pressure and reached a constant value of $\leq 10^{-7}$ A. Study of the N-2 sample revealed almost the same dependence of current on pressure ($I_{p,N-2} = 7 \cdot 10^{-7}$ A).

Powders (N-10) and (N-20) were obtained after treatment of the samples N-1 and N-2 in NaBH₄. They have a different silver content of 6.5% and 13.8%, and the initial currents (I_0) are $4 \cdot 10^{-5}$ A and $17 \cdot 10^{-5}$ A, respectively. After treatment of these samples in borate (which neutralized silver ions), the current in a sample with a low concentration of silver (N-10) also remained unsteady with a decrease in atmospheric pressure. In the sample with a high Ag content (N-20), the current

remained stationary as before, but the most important thing is the fact, that with a decrease in atmospheric pressure, the current did not decrease, but even increased significantly compared to the current before borate (NaBH_4) treatment (Table 1).

4. RESULTS AND DISCUSSION

As a result of processing the zeolite in a solution of AgNO_3 of various concentrations (0,02 M and 0,1 M), the following is observed:

1. An increase in the concentration of the AgNO_3 solution by 5 times led to a slight increase in the current ($I_{0\text{ N-2}}/I_{0\text{ N-1}} \sim 1,4$).

2. In sample N-1 in 25 minutes, the decreasing current value reached half of the primary value. With time, the current in the sample continued to decrease.

3. Over time, in the N-2 sample with a high silver concentration, the current value decreased to a certain stationary value (from 10,2 A to $12 \cdot 10^{-5}$ A).

The phenomena mentioned in paragraphs 2 and 3 can be explained as follows.

It is known that the presence of water promotes the transfer of ionic current in zeolites [7]. The introduction of silver ions into the zeolite led to their replacement of other positive ions in the zeolite

At a low concentration of silver ions (N-10), the current is carried by silver ions. With time (25 min), charge carriers are depleted and the sample volume is depleted. As a result, the current in sample N-10 is reduced to half of its primary value.

An increase in the concentration of silver in the zeolite (N-2) leads to the accumulation of charge (positive silver ions) at the ends of the sample and the neutralization of the charge due to the negative ions of the environment (A positive charge in the near-electrode regions is compensated by a negative charge on metal electrodes) Such compensation of positive and negative charges provides electro-neutrality of the system. Thus the Poisson condition is satisfied [14].

When a voltage is applied, an ion current flows in the sample due to the introduced silver ions. Since the concentration of injected silver ions is high, the current value ($7 \cdot 10^{-7}$ A) is maintained for a long time.

Processing of samples N-1 and N-2 revealed: the primary values of currents in samples N-10 and N-20 in comparison with samples N-1 and N-2, respectively, differ little (Table). Continuous measurements also showed a decrease in current in N-10 and a steady state in N-20.

The next stage of the study was to reduce the atmospheric pressure in the chamber. Studies have shown a decrease in the current value in samples N-1, N-2 and N-10 with a decrease in pressure from atmospheric to 0,1 Torr.

It is known that water molecules, being polarized, draw positive ions out of the pores of the negatively charged zeolite framework and ensure the passage of the ion current. When atmospheric pressure decreases, water evaporates (water vapor is removed), which leads to a decrease in the current value. As a result, positive ions stick to the walls of the pores, losing mobility, i.e., the ionic conductivity turns to zero.

An unusual result of the study is of interest - when the pressure decreases from p_{atm} to 0,1 Torr, the current value in the H-20 sample increased from $17 \cdot 10^{-5}$ to $13 \cdot 10^{-4}$ A. Probably, at low pressure neutral silver atoms become polarized and, like water molecules, contribute to the transfer of ionic current.

4. CONCLUSION

The electrical parameters of zeolite with different silver content were studied. The conductivity of the samples was studied by changing the pressure in the chamber.

It was found that at a low concentration of silver in the zeolite, the electrical conductivity decreases to 10^{-7} A as the air is pumped out to a pressure of 10^{-1} Torr.

At a high silver concentration, an increase in the current value in the range $17 \cdot 10^{-5} - 3 \cdot 10^{-4}$ A is due to the interaction of polarized silver atoms and positive ions in the negative zeolite framework. As a result of this interaction, the current transfer is carried out by the ions contained in the zeolite, and the silver atoms play the role of water molecules.

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