

Peculiarities of mass transfer and conductivity in silver-modified porous zeolite microstructure

B. G. SALAMOV^{a,*}, V. I. ORBUKH^b, N. N. LEBEDEVA^b, G. M. EYVAZOVA^c, Z. A. AGAMALIEV^c

^a*Department of Physics, Faculty of Sciences, Gazi University, 06500 Ankara, Turkey*

^b*Baku State University, Institute for Physical Problems, Baku, AZ 1148, Azerbaijan*

^c*Baku State University, Faculty of Physics, Nano Centre, Baku, AZ 1148, Azerbaijan*

This research work deals with the phenomenon of transfer of positive metal ions from the surface of a massive anode to the surface of the zeolite plate in an abnormally small external electric field E . The explanation of the observed phenomenon is based on the fact that in the electric field the conducting pores of the zeolite near the anode are charged with a negative charge localized on the walls of the zeolite pores. Since the pore diameter is significantly less than its length, these charges create an abnormally large local electric field on the anode surface. Thus, the electric field carried out the transfer of ions from the anode to the surface of the zeolite. Such type transfer mechanism is possible only from zeolite crystallites (constituting the zeolite plate), in which the pores are oriented perpendicular to the interface of the zeolite with the anode. Therefore, the distribution of the transferred substance on the surface of the zeolite is highly heterogeneous. Considerations that explain the threshold (i.e. the magnitude of the external electric field E) nature of the phenomenon are also considered. Thus, the obtained conductivity results indicate that silver-modified porous zeolite electrode can enable the system to operate with lower energy, enhanced mass transfer productivity, which may be useful in typical optoelectronic equipment used at atmospheric pressure.

(Received April 10, 2019; accepted August 16, 2021)

Keywords: Zeolite, Silver ions, Electric field, Mass transfer, Conductivity

1. Introduction

The phenomenon of mass transfer is widely discussed in the literature, since mass transfer accompanies various physical phenomena such as: electric welding, electric field modification of nanocomposites [1]; field desorption microscopy [2]; in porous bodies with a rigid frame [3]; in the study of the mechanical properties of crystals at nano indentation [4] and at the contact of chemically non-homogeneous minerals [5]. For evaluating mass transfer in complex systems, the technique of NMR has proved to be the most versatile and sensitive tool [6,7]. NMR allows recording the redistribution rate of the molecules within the sample over distances of typically micrometers, without any interference with the intrinsic processes of molecular propagation. In the case of zeolites [8], NMR technique has given rise to extendedly view on the guest mobility in zeolite micro pores [9]. The diffusivities were found to exceed previously measured values by even as much as several orders of magnitude. Today, in many cases these differences may be attributed to the existence of additional transport resistances like surface barriers [10] and/or transport resistances in the zeolite bulk phase [11,12] acting in addition to the diffusion resistance of the genuine micropore space [13]. The techniques of molecular modeling, exactly reproduced the diffusivity data determined by NMR [14,15] and established that mass transfer occurs under the sole influence of the genuine pore space.

This research work presents the mass transfer of ions from the surface of a massive metal electrode - anode to the surface of a mechanically pressed plate of zeolite-clinoptilolite (CL). In this regard, the work on "surface ionization" [16-19] was considered, as a result of which positive and negative ions are formed on the surfaces of bodies when atoms and molecules evaporate from them. In the monograph [20], for the first time, the results of experimental studies of surface ionization are systematized. At the same time, the basic theoretical concepts are given by Knat'ko et.al. in [21] and the results of the study of surface ionization of alkali metal atoms and organic molecules on the surface of gold intermetallic significantly expand the concept of the phenomenon. As it can be seen from the review of the above works, ionization requires heating the surface. However, there is a possibility of mass transfer of ions from the non-heated metal surface under the effect of strong (10^8 V/cm) electric fields [22-26]. Strong electric fields became available for quantitative work as a result of the use of needle - shaped auto electronic emitters, this led to the discovery of a new desorption effect by an electric field. Field desorption is the emission of ions under the effect of an electric field. Theoretical estimates of desorption field strength for different metals are in the range 1428-288 MV/cm. All of the above conditions are not implemented in our case. In this study, for the first time, the mass transfer of metal ions from the non-heated surface of a massive anode to the surface of a zeolite plate pressed is observed when a sufficiently weak ($U_o = 50$ V) constant electric field is

applied. We believe that this is possible due to the properties of zeolite.

The examined $(\text{Ca}, \text{K}_2, \text{Na}_2, \text{Mg})_4\text{A}_{18}\text{Si}_{40}\text{O}_{96} \cdot 24\text{H}_2\text{O}$ zeolite-clinoptilolite [27] is an aluminosilicate framework, the structure of which is formed at the junction of the $[\text{AlO}_4]^{5-}$ and $[\text{SiO}_4]^{4-}$ tetrahedrals with common vertices. Since Al and Si have unequal valences, cations (usually Na^+ , K^+ , Ca^{2+} , Mg^{2+}) which are not placed in the crystal lattice, but on the inner surface of channels and cavities (near aluminosilicate tetrahedra), are part of this zeolite. At the same time, they migrate and plays an important role in adsorption, ion exchange and electrical conductivity. Under normal conditions, the intracrystalline channels are filled with water wetting their walls. The number of molecules of zeolitic water N is determined by the volume of free intra crystalline space and can reach 28-34 per unit cell [27]. Due to a well-developed inner surface, the conductivity of a clinoptilolite is of a volumetric nature [28]. However, when studying electrical conductivity in atmospheric conditions, the contribution of surface conductivity cannot be neglected.

In these studies of current at a constant voltage, either a steady-state current is observed, which is not characteristic of ionic conductivity or a continuously falling current. Therefore, the question of the existence of volume ionic conductivity of zeolites at a constant voltage is debatable. In this work, we present the kinetics of the establishment of a steady-state current in the constant-voltage regime, which is unusual for ionic conductivity, in the clinoptilolite plate modified with silver ions. Observed in the present work, the transfer of anode substance to the surface of the zeolite plate is due to the formation of fixed negative charge concentrated on the randomly oriented crystallites of the zeolite. The transfer of the electrode mass is carried out in small areas of the zeolite surface where the electric field is large.

2. Experimental

2.1. Characterization of Zeolite Materials

The examined Ca-CL sample has monoclinic structure and following unit cell parameters: $a=1.7627$ nm, $b=1.7955$ nm, $c=0.7399$ nm, $\beta=116$. The average crystal size of the examined CL sample is 8-10 nm. Our results are in good agreement with the literature data [29]. XRD measurement indicates that high crystalline is the result of the peak intensity and sharpness [30]. Channels *A*, *B* and *C* have the sections, 0.72×0.44 nm; 0.47×0.41 nm, and 0.55×0.4 nm respectively. It should be noted that in clinoptilolite, these channels are predominantly occupied by exchangeable mobile (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) cations and H_2O . The samples of porous clinoptilolite $(\text{Ca}, \text{K}_2, \text{Na}_2, \text{Mg})_4\text{A}_{18}\text{Si}_{40}\text{O}_{96} \cdot 24\text{H}_2\text{O}$ [32,33] are aluminosilicate with the following structure and skeleton composition: SiO_2 65-72%, Al_2O_3 10-12%, CaO 2.4-3.7%, K_2O 2.5-3.8%, Fe_2O_3 0.7-1.9%, MgO 0.9-1.2%, Na_2O 0.1-0.5%, MnO 0-0.08%, Cr_2O_3 0-0.01%, P_2O_5 0.02-0.03%, $\text{SiO}_2/\text{Al}_2\text{O}_3$ 5.4-7.2%. The dielectric zeolite samples (ZS)

are cut from a single block of natural zeolite mineral (i.e. diameter $d = 22$ mm, thickness $l = 2$ mm). Comprehensive information concerning location, arrangement and chemical composition of the natural zeolite ($\rho \sim 10^{11}$ $\Omega \cdot \text{cm}$) is presented in section 3.1 [31,34].

The morphological and compositional analyses of zeolite wafers are analyzed by SEM modulated energy dispersive X-ray spectroscopy (SEM/EDX). The values of current are recorded in the short-circuit mode with a sensitive high-precision digital voltmeter–electrometer. The accuracy in the measurement of electric currents is equal to 10-15 A. The obtained data is recorded into a PC from an analog-to-digital converter and processed using standard statistical methods. Studies of the elemental mapping and the spectra of EDX for measured clinoptilolite wafers showed that the unmodified zeolite sample has the highest content (9.93%) of Ca ions. Fig. 1 demonstrate SEM image corresponding to the characteristic morphologies of the Ca-clinoptilolite material.

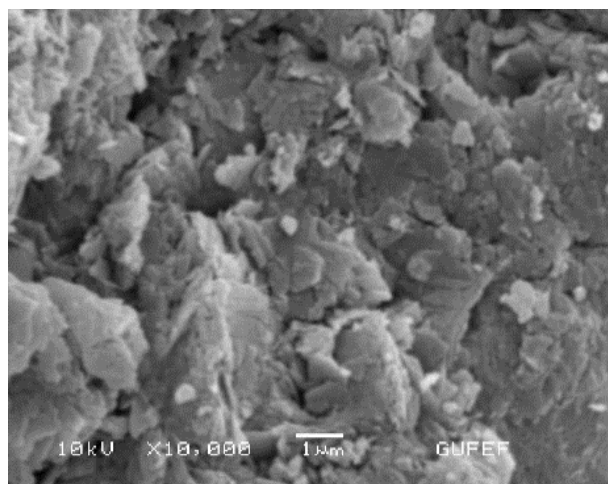


Fig. 1. SEM image of the Ca-clinoptilolite sample

SEM studies have revealed that samples of zeolite tuffs mainly have a complex micro surface relief formed by microcrystals and aggregates of various mineral phases. In most cases, monomineral aggregates of zeolites are weakly crystallized masses or microcrystals. Aggregates of micro-crystals are concentrated in microrodes and in micro cracks, which are fairly uniformly distributed over the surface of the sample. Clinoptilolite crystals have a lamellar form.

2.2. Measurement method

To conduct conductivity measurements, silver-modified zeolite Ag^+ -CL samples were prepared by the ion-exchange method according to a previously reported procedure (see [35]). The zeolite plate was immersed for 24 hours at room temperature in a 0.02 M solution of silver nitrate (AgNO_3), then washed in deionized water

and dried at 100 °C. To study the transfer of positive metal ions from the surface of a massive anode to the surface of a zeolite plate in an external electric field, we used samples subjected to ion exchange in an AgNO_3 solution. This was recorded during the elemental composition study of the zeolite plates analyzed by field emission SEM (JEOL JSM7600F). Fig. 2 shows the total spectrum of the map before (a) and after (b) silver ion modification of the zeolite, where it can be seen how Ag ions replaces Ca ions in the pores of the CL.

Such a modified plate was placed in a cassette, where it was clamped between two flat polished copper and AISI 304 stainless steel electrode discs. This is a complex alloy of stainless steel, which contains elements such as Cr (18-

20%), Ni (8-11%). The stainless steel electrode was an anode. A dc feeding voltage $U_f = 50$ V was applied to the electrodes from a stabilized power source. The current in the sandwich mode was measured at room temperature in atmospheric air and at a humidity of 80%. A constant voltage of 50 V was applied to the electrodes (for detailed information see [36]) and the current slowly increased over time and reached a steady state value of 3×10^{-4} A. We attribute the increase in current to the interaction of silver ions with zeolitic water, which leads to an increase in the mobility and, as a consequence, to an increase in the current. After that, a stationary current is observed (see Fig. 3) and it becomes possible to measure the I-V characteristic (see Fig. 4).

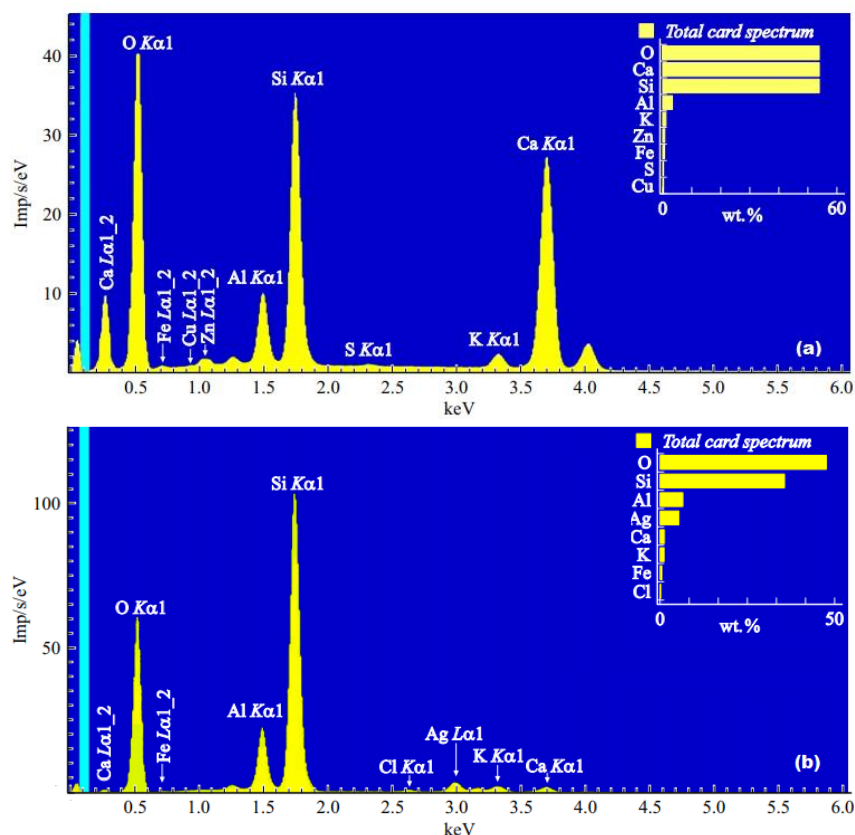


Fig. 2. EDS spectra for pure (a) and silver-modified zeolite (b) plate (color online)

Latest studies on the current kinetics demonstrated that the current varies rapidly with time for several seconds after the charging of the cell with zeolite plate. The nature of the current kinetics has changed as a function of the current direction and magnitude [33]. The current dynamic behavior indicated that the current value and stability changed significantly with feeding voltage U_f during the time range of 150 s across various regions of voltages. Zeolite and atmospheric air are electrically insulated by specific voltage value and cations (especially Na^+ , K^+ , Ca^{2+} , Mg^{2+}) that are important in the ionic conduction (cations motion) causing the non-monotonic current oscillations with microampere amplitude. The density and structure of zeolite water strongly depends on electric field. A number of Na^+ ions were found to pass

through the pore and reduced the electric field in the pore for porous materials [34]. This motion caused a significant influence on the behavior of the H_2O . In each ion transition, the number $n\text{H}_2\text{O}$ of water molecules inside the pore decreases. It should be noted that with a decrease in atmospheric pressure, the zeolite plate modified with Ag ions again becomes highly-resistance due to the loss of water vapor [36].

Fig. 4 shows the current-voltage characteristic hysteresis, which can be explained by the electret phenomenon associated with the presence of a gap between the zeolite and the anode [37]. With the forward increment and reverse decrement feeding voltages, measured dates for natural CL demonstrated an increase and extended range of the hysteresis loop at atmospheric

pressure under feeding voltage from ± 50 V to ± 200 V (see Fig. 4). For silver-modified zeolite Ag^+ -CL the range of hysteresis loop considerably depends on the feeding voltages and pressure.

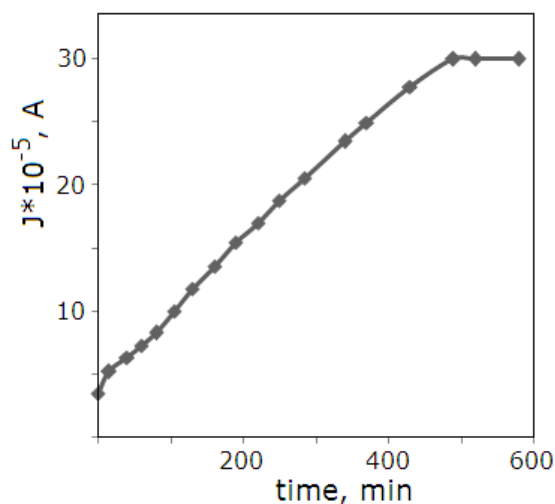


Fig. 3. The dependence of current on time after switching on the DC feeding voltage $U_f = 50$ V

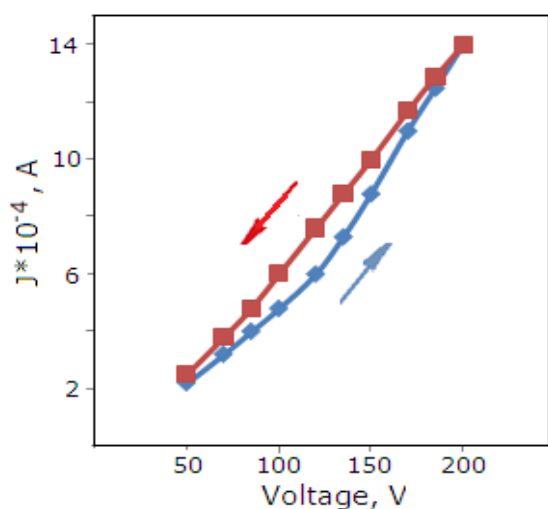


Fig. 4. I-V characteristic for saturation current, when the voltage increases from 50 V to 200 V and decreases from 200 V to 50 V (color online)

According to Fig. 4, the slope of Ag^+ -CL is higher than for unmodified CLs for a wide pressure range, which suggests that Ag modification is the cause of the increase of conductivity in terms of CL electrodes. Higher current values were observed at the lower voltage values in the silver-modified porous zeolite electrodes. The charge transport through the modified CL layer significantly affects the characterization of the modified CL electrode material. A microporous structure with exchangeable cations in this modified layer can bring about extra diffusion properties, and the charge transport process is complicated to some extent [40]. The anionic framework might be in interaction with the Ag^+ cations in the zeolite

in comparison with the Na^+ and K^+ cations, due to their higher charge density [41,42]. Therefore, Na^+ and K^+ ions with larger ionic radii may be holding weakly onto the anionic framework with the increasing pressure, and, thus, they are easily released from their sites, allowing them to be looser and easier to maneuver in order to facilitate their conductivity.

These results suggest that the conductivity of CL can be adjusted by adjusting U_f and pressure, which has a direct effect on expanding the range of the mass transfer. It can be speculated that, with the increase of pressure, the cation mobility with the interaction of the framework water and charge balancing cations results in an increase since the cation and lattice attractions decrease, which might contribute to the cationic transport [32,43]. It is presented in [44, 45] that the conductivity of A-type zeolites was growing with the negative activation volume of conduction, which includes the electronic conduction, like metal or semiconductor materials. However, it has been stated that the electronic conduction processes in zeolites are incoherent at low pressures [41]. The Ag ions are in interaction with the anionic lattice because of their greater charge density in comparison with the Na^+ and K^+ . Thus, the cations with the largest ion radii are removed from their location with the increasing of pressure for the development of conductivity. Pressure leads to an increase in diffusion in the crossing channels with a decreased volume with the increasing of pressure and alterations in the cation-lattice interaction. At the same time, this effect consists of novel passages for the cations into the intracrystalline volume to provide the development of conductivity. These effects or their combinations become important for the development of conductivity under pressure. Our results show that the effect of pressure on the conductivity can be evaluated with the following considerations: the conductivity of the mobile positive ions into the pores of the zeolite material increases because of the molecules' interaction [33]. Furthermore, the conductivity of the positive ions decreases because the scattering in their energy increases at atmospheric pressure [35]. There is an agreement between these conduction results and data presented in [32,46,47].

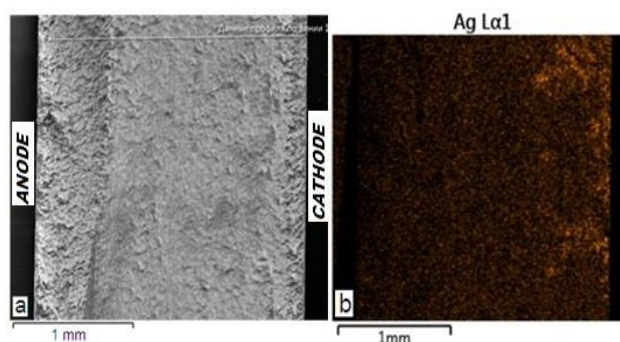


Fig. 5. Morphology of (a) a cross section for silver-modified zeolite plate and elemental mapping (b) after the passage of current

As a result of the passage of current, positive silver ions accumulate at the end of the plate facing the copper electrode-cathode. This is illustrated in Fig. 5, which shows the morphology of the cross section of the plate thickness from the end adjacent to the anode (left edge) to the end adjacent to the cathode (right edge).

A negative charge is formed at the opposite end of the plate facing the stainless steel anode. It turned out that as a result of a long (10 hours) passage of a small (10^{-4} A)

current, ions from the stainless steel anode passed to the surface of the zeolite plate. Specially carried out measurements have established that at small values of the exposure time the mass transfer was not observed. In other words, mass transfer has a threshold character. Fig. 5 shows a photograph of the surface of a zeolite plate modified with silver ions facing the anode after current has passed.

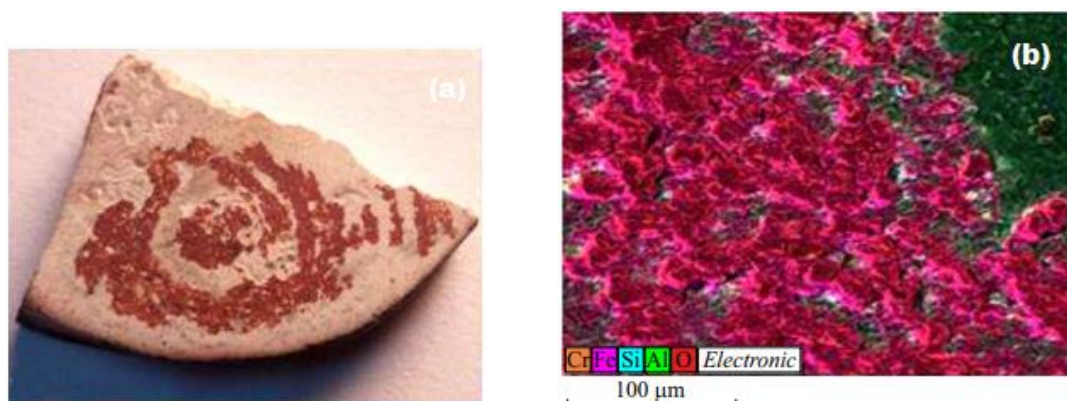


Fig. 6. Image of surface (a) and elemental mapping (b) for silver-modified zeolite plate after passing current (color online)

Fig. 7 presents the total spectrum of the map on the surface area of a zeolite with ions from the anode (i.e. after passing current).

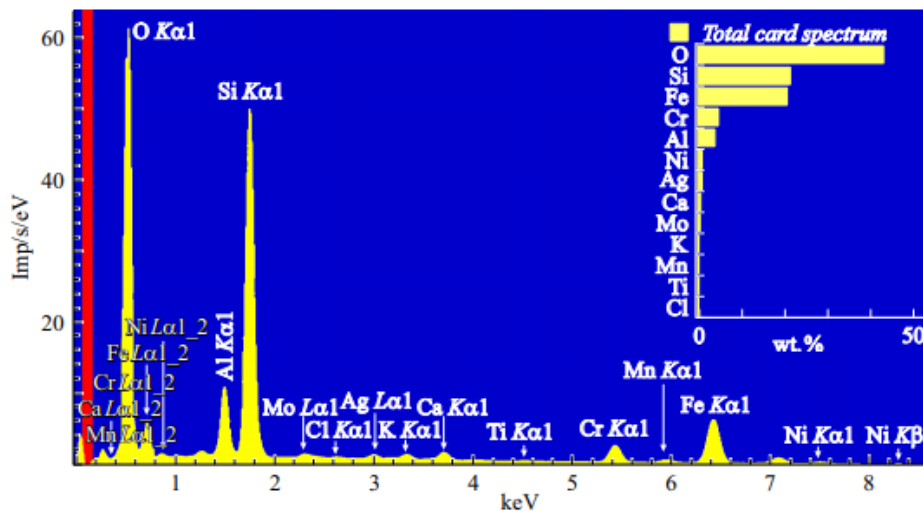


Fig. 7. EDS spectra for the silver-modified zeolite surface with ions from the anode (color online)

Comparison of Fig. 2 and Fig. 7 shows that iron and chromium ions, which AISI 304 stainless steel contains, have passed from anode to zeolite. It is seen that ions pass to the zeolite surface from local areas on the anode rather than from the entire area of the contact. We also note that the ion transfer intensity significantly depends on the exposure time in the electric field.

3. Results

3.1. Characterization of zeolite

The chemical composition of the clinoptilolite $(Ca, K_2, Na_2, Mg)_4A_{18}Si_{40}O_{96} \cdot 24 H_2O$ samples studied in the work are presented in Table 1.

Table 1. The SEM-EDX determined chemical composition of un-modified zeolite (A) and silver-modified clinoptilolite $Ag^+ - CL$ (B)

	Zeolite A	Zeolite B
Elements	Wt. %	Wt. %
O	46.33	48.21
Mg	0.70	1.77
Al	7.38	6.05
Si	39.10	26.23
K	2.31	1.50
Ca	9.93	1.92
Fe	1.15	0.98
Cu	0.00	0.30
Zn	1.00	0.00
Ag	0.00	5.94
Na	0.09	1.77
Si/Al	5.30	4.30

Analysis of the chemical composition of the studied samples showed a Si/Al ratio < 5 , which is peculiarity of this type of zeolite [38] (Table 1). Among the exchangeable cations, Ca^{2+} predominates; it accounts for about 60% of the mass of the total number of cations of all types, some of which, in decreasing order of their content, can be represented as: $Ca > K > Mg > Na$. In nature, the predominance of one or another type of exchange cation in a zeolite is determined by the nature of its ion-exchange interaction with groundwater. The increase in the content of the incoming cation occurs in proportion to the initial concentration of the solution and the time of its interaction with the solid phase of the zeolite. It was found experimentally that Na^+ and K^+ ions quite easily enter in the channels and cavities of the clinoptilolite framework and, under certain conditions, can realize up to 90% of its maximum ion-exchange capacity. These cations replace bivalent ions Ca^{2+} and Mg^{2+} during of ion-exchange reactions: $Na^+(K^+) \rightarrow 1/2 Ca^{2+}$, $Na^+(K^+) \rightarrow 1/2 Mg^{2+}$.

The type of predominant extraframework cations has a significant effect on the electrical and thermal behavior of the zeolite, the exchange of which can significantly change its dielectric response [36-37]. Because, the exchange of positive ions between various crystallites takes place during thermal state equilibrium in the zeolite plate. The substitution occurs between the same types of ions during the usual ion-exchange process in the pores of the zeolite. The same exchange process occurs at thermal equilibrium conditions in the zeolite plate, but it becomes between identical ions. This does not lead to new phenomena in the absence of the external electric field. The same exchange in the identical ions between different crystallites provides a continuous ionic current [39] in an external electric field at the measurement of electrical conductivity.

We explain the experimentally observed mass transfer by ion field emission from the metal anode surface. This phenomenon is possible only in very strong (10^7 – 10^8 V/cm) electric fields. Such strong fields occur (briefly) on non-homogeneities with a small radius of curvature. The

negative charge on the surface of the zeolite is distributed quite heterogeneous. This charge is a negative stationary charge on the walls of zeolite pores. In the depth of the plate, this negative charge is compensated by positive charges freely moving in the zeolite pores. Therefore, during the transfer of positive metal ions from the surface of a massive anode to the surface of the zeolite plate in the pores formed uncompensated negative charge. This stationary charge, localized (in pores) at the pore exit to the surface of the zeolite plate, creates a field that can cause ionic field emission from the anode. The fact is that the pore diameter is 0.4 - 0.6 nm, that is significantly less than the pore length (coinciding with the size of the zeolite crystallite from 0.5 to 30 μm). The resulting local electric field on the anode surface significantly lowers the barrier with respect to the output of a positive ion from the anode material.

3.2. Mass transfer and theoretical model

To explain the threshold nature of the observed phenomenon, we will proceed from a simple model consisting of a zeolite plate separated by a gap from the metal electrode. The conductivity of zeolite is associated with the movement of positive ions in the pores of the zeolite. Therefore, in the course of current flow on the surface of the zeolite plate (from the anode side) a fixed negative charge is formed, localized on the pore walls, where its value is $q_o = J \cdot t$ (where J - is the current value, t - is the current flow time).

At the same time, exactly the same positive charge is induced on the anode surface, which is realized by the ions of the anode material. The capacitance of such a capacitor is $C = \epsilon_o S/d$ (where S is the surface area, d is the distance between the zeolite plate and the electrode. The difference between the ion binding energy on the anode surface and the binding energy of the same ion on the surface of the zeolite plate is denoted in eV as Δ .

The aim of this work is to study the stability of the described system with respect to transfer part of the electrode ions from the surface of the anode to the surface of the zeolite plate. Let q denote the value of the charge transferred, as a result of this instability, from the anode to the zeolite. Then the total energy of our system $W(q)$ has the form:

$$W(q) = \frac{(-q_o + q)^2}{2C} + \frac{q\Delta}{e} \quad (1)$$

where $e = 1.6 \cdot 10^{-19}$ C is the elementary charge. The first term in (1) is the energy of the electric field in the gap, the second is the increase in energy due to the transfer of a part of the charge q . Note that, in connection with this charge transfer, the first term decreases due to a decrease in the total charge $(-q_o + q)$ on opposite surfaces.

The steady state (which is observed experimentally) corresponds to the minimum of the total energy (1). Equate the derivative of energy (1) to zero:

$$\frac{dW(q)}{dq} = 0 \quad (2)$$

From (2) we get:

$$q = q_0 - \frac{C\Delta}{e} \quad (3)$$

Considering that $q_0 = J \cdot t$ we rewrite formula (3) as:

$$q = Jt - \frac{C\Delta}{e} \quad (4)$$

The mass of the electrode substance transferred to the zeolite surface (taking into account the ratio $M = m_o q/e$)

$$M = \frac{m_o}{e} \left(Jt - \frac{C\Delta}{e} \right) \quad (5)$$

where m_o – is ion mass.

Since the mass of the transferred substance (5) is positive, therefore at negative Δ values, the threshold character is absent. At the same time, at positive Δ , formula (5) has a threshold character.

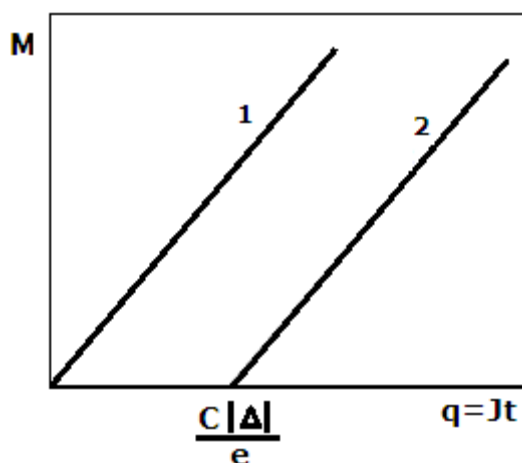


Fig. 8. The dependence of the mass M of the substance deposited on the zeolite surface from the carried charge:

1 - $\Delta < 0$; 2 - $\Delta > 0$

From formula (5) it can be understood that the mass of the substance transferred to the zeolite, as a function of the charge $q_0 = J \cdot t$, has a threshold character. If the expression in brackets in (5) is negative, then ($M = 0$) there is no mass transfer. When the expression in parentheses becomes positive, then mass transfer takes place (i.e. the binding energy of the ion of the anode material at the anode itself is greater than its energy on the surface of the zeolite). In the opposite case, when Δ is negative, as can be seen from (5), it does not have a threshold character (in formula 5, the expression in parenthesis is always positive). Since in our experiment the threshold was fixed in relation to mass transfer, we conclude that Δ is positive.

4. Conclusions

The observed mass transfer from the metal anode to the surface of the zeolite indicates a substantially non-uniform distribution of the electric field at the contact of the porous ionic material with the metal (in some areas the field is sufficient for ion emission). The explanation of mass transfer is based on a decrease in the binding energy of the ion on the electrode due to the anomalously large local electric field (10^7 – 10^8 V/cm) created by the fixed negative charge of the zeolite pores. It is shown that the threshold value of this charge, at which mass transfer begins, is proportional to the capacity of the gap between the zeolite and the anode. The configuration considered in this paper is not the only one in which significant electric fields appear. For example, these fields can affect the conductivity of zeolite powders and wafers. The emission model proposed in this work explains the threshold nature of mass transfer, as a function of charge, at the electrode gap. This charge is formed as a result of the flow of current. The threshold value of the accumulated charge, as can be seen from (5), is equal to $\frac{C\Delta}{e}$. Moreover, it was

established that the threshold nature of this dependence is possible only if the binding energy of the emitted ion with the anode material is greater than its zeolite counterpart.

We hope our results may help to describe physical mechanisms of the charge transport phenomenon of the typical optoelectronic equipment used at atmospheric pressure. We believe that our novel results can have an influence in electro-optical properties of the gas discharge microstructure with high performance alumino-silicate materials acting as promising plasma light sources with large emitting area.

References

- [1] M. Saqib, F. Ali, I. Khan, N. A. Sheikh, *Neural Computing and Applications* **30**, 2159 (2018).
- [2] J. H. Gross, *European Journal of Mass Spectrometry* **26**(4), 241 (2020).
- [3] Ch. Liu, M. Pan, L. Zheng, P. Lin, *International Communications Heat Mass Transfer* **110**, doi.org/10.1016/j.icheatmasstransfer.2019.104434 (2020).
- [4] Z. K. Saralidze, M. V. Galustashvili, D. G. Driaev, *Physics of the Solid State* **48**(7), 1298 (2006).
- [5] W. Fan, M. A. Snyder, S. Kumar, P.-S. Lee, W. C. Yoo, A. V. McCormick, R. L. Penn, A. Stein, M. Tsapatsis, *Nat. Mater.* **7**, 984 (2008).
- [6] N. Robinson, C. D'Agostino, *Topics in Catalysis* **63**, 319 (2020).
- [7] P. T. Callaghan, *Translational Dynamics and Magnetic Resonance*; Oxford University Press: Oxford, UK, 2011.
- [8] J. Kärger, J. Caro, *J. Chem. Soc. Faraday Trans. I* **73**, 1363 (1977).
- [9] Z. Zhaoa, X Lic, S. Lia, S. Xub, X. Baob, Y. Bilged, P. Andrei-Nicolaed, M. Ulrichd, W. Zhanga,

- Microporous Mesoporous Mater. **288**, 109555 (2019).
- [10] F. Hibbe, C. Chmelik, L. Heinke, J. Li, D. M. Ruthven, D. Tzoulaki, J. Kärger, *J. Am. Chem. Soc.* **133**, 2804 (2011).
- [11] S. Vasenkov, W. Böhlmann, P. Galvosas, O. Geier, H. Liu, J. Kärger, *J. Phys. Chem. B* **105**, 5922 (2001).
- [12] S. Vasenkov, J. Kärger, *Microporous Mesoporous Mat.* **55**, 139 (2002).
- [13] D. M. Ruthven, Fundamentals of adsorption equilibrium and kinetics in microporous solids. In *Adsorption and Diffusion: Science and Technology – Molecular Sieves*; H. G. Karge, J. Weitkamp, Eds.; Springer: Berlin, Germany **7**, 1 (2008).
- [14] S. Fritzsche, R. Haberlandt, J. Kärger, H. Pfeifer, M. Wolfsberger, *Chem. Phys. Lett.* **171**, 109 (1990).
- [15] R. Haberlandt, S. Fritzsche, H.-L. Vörtler, Simulation of microporous systems: Confined fluids in equilibrium and diffusion in zeolites. In *Handbook of Surfaces and Interfaces of Materials*; H.S. Nalwa, Ed.; Academic Press: New York, NY, USA **5**, 357 (2001).
- [16] M. Wiśniewska, T. Urban, S. Chibowski, G. Fijałkow- Ska, M. Medykowska, A. Nosal-Wiercińska, W. Franus, R. Panek, K. Szewczuk-Karpisz, *Applied Nanoscience* **10**, 4475 (2020).
- [17] V. J. Inglezakis, A. Satayeva, A. Yagofarova, Z. Taa-nov, K. Meiramkulova, J. Farrando-Pérez, J. C. Bear, *Nanomaterials* **10**, 1156 (2020).
- [18] J. Kärger, D. M. Ruthven, D. N. Theodorou, *Diffusion in Nanoporous Materials*; Wiley-VCH: Weinheim, Germany, 2012.
- [19] N. Y. Chen, T. F. Degnan, C. M. Smith, *Molecular Transport and Reaction in Zeolites*; Wiley-VCH: New York, NY, USA, 1994.
- [20] E. Ya. Zanberg, N. I. Ionov, *Surface ionization*, Nauka, 1969, 432 (in Russian).
- [21] M. V. Knat'ko, M. N. Lapushkin, *Technical Physics* **83**(6), 51 (2013).
- [22] L. Zigan, *Energies* **11**(6), 1361 (2018).
- [23] E. W. Muller, *J. Appl. Phys.* **27**, 474 (1956).
- [24] F. J. Keil, R. Krishna, M. O. Coppens, *Rev. Chem. Eng.* **16**, 71 (2000).
- [25] D. P. Bernatskii, Yu. A. Vlasov, *Sov. Phys. Technical Phys.* **57**(11), 2257 (1987).
- [26] V. N. Ageev, D. P. Bernatskii, Y. A. Kuznetsov, V. G. Pavlov, N. D. Potekhina, B. V. Yakshinskii, *Phys. Low. - Dim. Struct.* **7**, 51 (1994).
- [27] G. Gottardi, E. Galli, *Natural Zeolites, Minerals and Rocks Series*, Berlin: Springer-Verlag **18**, 409 (1985).
- [28] Ch. Baerlocher, W. M. Meier, D. H. Olson, *Atlas of Zeolite Framework Types*, Revised Amsterdam: Elsevier 2001.
- [29] B. G. Salamov, Kurt H. Hilal, *JOM Miner. Met. Mater. Soc.* **72**(2), 644 (2020).
- [30] S. V. Baryshnikov, S. V. Lankin, E. V. Stukova, V. V. Yurkov, *Sovrem. Nauk. Tehnol.* **6**, 26 (2004).
- [31] J. Kalogeras, A. Vassilikou-Dova, *Cryst. Res. Technol.* **31**(6), 693 (1996).
- [32] B. G. Salamov, *Advances in Optoelectronic Materials. Advances in Material Research and Technology*. In: S. J. Ikhmayies, H. H. Kurt (eds), Springer, Cham. doi.org/ 10.1007/978-3-030-57737-7_7, 175-209, 2021.
- [33] S. Ozturk Koc, K. Koseoglu, S. Galioglu, B. Akata, B. G. Salamov, *Microporous Mesoporous Mater.* **223**, 18 (2016).
- [34] V. A. Evdokimova, L. P. Karatsuba, S. V. Lankin, *Perspektivnye Materially* **5**, 340 (2007).
- [35] S. Ozturk Koc, S. Galioglu, S. Ozturk, B. Akata, E. Koc, B. G. Salamov, *J. Electronic Materials* **47**(5), 2791 (2018).
- [36] U. Bunyatova, S. Ozturk Koc, V. Orbukh, G. Eyvazova, Z. Agamaliyev, N. Lebedeva, I. C. Koçum, B. G. Salamov, M. Ozer, *Superlattices and Microstructures* **98**, 295 (2016).
- [37] U. Bunyatova, V. Orbukh, G. Eyvazova, N. Lebedeva, Z. A. Agamaliyev, I. C. Kocum, M. Ozer, B. G. Salamov, *Superlattice. Microstruct.* **111**, 1203 (2017).
- [38] A. K. Jonscher, A. R. Haidar, *J. Chem. Soc. Faraday, Trans. I* **82**(12), 3553 (1986).
- [39] S. Yu. Davydov, *Phys. Solid State* **51**(4), 849 (2009).
- [40] S. Galioglu, M. Isler, Z. Demircioglu, M. Koc, F. Vocanson, N. Destouches, R. Turan, B. Akata, *Microporous Mesoporous Mater.* **196**, 136 (2014).
- [41] D. R. Rolison, *Chem. Rev.* **90**, 867 (1990).
- [42] S. Galioglu, M. Zahmakıran, Y. E. Kalay, S. Ozkar, B. Akata, *Microporous Mesoporous Mater.* **159**, 1 (2012).
- [43] S. V. Goryainov, R. A. Secco, Y. Huang, H. Liu, *Phys. B* **390**, 356 (2007).
- [44] M. D. Rutter, R. A. Secco, Y. Huang, *Chem. Phys. Lett.* **331**, 189 (2000).
- [45] K. M. Ault, R. A. Secco, *Solid State Ion.* **89**, 37 (1996).
- [46] R. A. Secco, E. A. Secco, *Phys. Rev. B* **56**, 3099 (1997).
- [47] B. G. Salamov, Kurt H. Hilal, *JOM Miner. Met. Mater. Soc.* **73**(5), 1271 (2021).