

GAS DISCHARGE DEVICE BASED ON THE POROUS ZEOLITE MICROSTRUCTURE

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The stabilization of glow microdischarges in a *dc* air cold plasma is studied experimentally functions of pressure p (18-760 Torr) and interelectrode distances d (50-250 μm) in the gas discharge electronic device (*GDED*) with nanoporous zeolite cathode modified by Ag nanoparticles (resistivity $\sim 10^{11}$ - $10^6 \Omega\cdot\text{cm}$). Comparison of current and discharge light emission (*DLE*) from glow microdischarges are used for the determination of the stabilization under low- and atmospheric pressure conditions. It is found that the gas *DLE* inside the nanoporous zeolites develop from the surface if the amplitude of the applied voltage reaches given threshold. Moreover, uniform *DLE* can be generated in air up to atmosphere pressure. It is also shown that breakdown voltage U_B is reduced significantly at atmospheric pressure when zeolite cathode modified by Ag nanoparticles is used. Due to the very small electrode gap width we can describe the behaviour of the charged particles in the electric field of our system with the *dc* Townsend breakdown theory, depending on the pressure range. The generation and maintenance of stable cold plasma is studied according to the effect of Ag nanoparticles.

Keywords: nanoparticles, atmospheric pressure plasma, conductivity mechanisms, electrical properties, nanoporous zeolite

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1. INTRODUCTION

There is growing interest in non-thermal plasma processing techniques optimized for atmospheric pressure applications due to their significant industrial advantages. At atmospheric pressure, thin film deposition at very high rates is possible, and cost-intensive vacuum technology can be avoided. Many approaches have been proposed in the last 15 years to overcome the problems of generating and sustaining a stable, uniform and homogeneous non-thermal atmospheric pressure (*AP*) plasma [1,2].

In spite of intensive research in the field of metal nanoparticles (NPs) and clusters, the problem of proper size-control and materials fabrication with particles of the desired properties still exists, because each type of material requires new approach for the development of appropriate synthesis conditions of clusters and NPs [3]. In that sense, the physico-chemical interaction between plasma and the loaded active metals, such as silver NPs [4] is still not well understood. For that purpose, using nanoporous materials, such as zeolites, modified with active metal NPs can be an alternative to clarify the possibilities of using these materials in practical plasma applications. Considering availability of strong effect of metal NPs and especially silver on discharge plasma of gas discharge electronic device (*GDED*), further experimental studies are needed to provide insight into the physico-chemical processes influencing the plasma characteristics and cathode properties.

Operating efficiently of the system will be based on the use of zeolite cathode (*ZC*), which is a good absorber of gas molecules in their nanoporous. The electrode dimensions, especially the electrode gap width d in the micrometer range, are small enough to generate sufficiently high electric field strengths to ignite *AP* glow

discharges applying *dc* voltages (less than 1.5 kV). With this last type of *GDED* plasma can be generated in air at *AP*. For these reasons, it is important to know the relation between the geometrical parameters and the discharge characteristics from the viewpoint of the cell optimization.

Deliberate modification of electrode surfaces with zeolites has evoked considerable interest. The attractive zeolite characteristics that are liable to affect the electron transfer reactions at an electrode-discharge interphase are (a) the size and shape selectivity due to the rigid structure made of pores and channels of molecular dimensions; (b) the cation-exchange capacity arising from the charge compensation of the negatively charged aluminosilicate lattice by mobile extra framework cations; and (c) the catalytic properties of both intrinsic and extrinsic sites of the microporous materials. This has led to the design, preparation, and use of various zeolite-modified electrodes.

The zeolite frameworks are formed by chains of *Si* and *Al* anionites. The framework has a negative charge because of its structure and this charge is compensated by water molecules and cations of alkali and alkali-earth metals Ca, K, Na, Mg weakly connected with it. Water can be removed by heating or evacuation of the zeolite, which has no effect on a rigid framework, its structure is virtually unchanged. The zeolite pores have the right forms. Connecting between each other through "windows" (0.26-0.27 nm), they form the perforated channel chain. That's why the zeolites can be considered as the object on which besides well-known phenomena (adsorption, ion-exchange phenomena), investigate the electron porous emission, electron multiplication and gas discharge in pores, dielectric and electric properties at pore saturation by different gases and liquids. Consequently, the peculiarities of plasma generation in

the GDED system with Ag-modified metal nanoparticles in this study we investigate the enhanced efficiency of Ag⁰-ZC on the fundamental characteristics of GDED. Besides operation at AP, in this study we showed that Ag⁰-ZC is an effective material for reducing the break-down voltage (U_B) substantially and charge transport occurs at lower voltages with respect to un-modified ZC.

2. EXPERIMENTAL

The behaviour of the current-voltage characteristic (CVC) of the discharge cell with ZC is determined by the type of the discharge. Therefore CVCs of the ZC plate were taken at different residual pressures and the GDLE from the pores was simultaneously detected. Natural zeolite was taken as a porous object. Zeolites are non-stoichiometric compounds, the compositions of which vary over wide limits and produce a series of solid solutions. Zeolites are aqueous alumo-silicates in which an infinite alumosilicate frame is produced by [SiO₄]⁴⁻ and [AlO₄]⁵⁻ tetrahedra having common vertices. These tetrahedra have communicating cavities occupied by large ions and water molecules [5]. Clinoptilolite is the most abundant of the natural zeolites [6], but composition and purity vary widely among the many deposits found throughout the world. For our study we used (Ca,K₂,Na₂,Mg)₄Al₈Si₄₀O₉₆×24H₂O the clinoptilolite from Western Turkey deposit in Gordes Manisa. This natural zeolitic material contains on average 90-95% of the clinoptilolite zeolitic mineral [7,8]. Clinoptilolite belongs to a class of zeolite minerals having the clear-cut structural topology of heulandite (HEU) and the ratio of Si/Al > 4.0. The structural topology of the HEU tetrahedral lattice is well understood. At the same time, Fig. 1 shows the SEM-EDX analyses composition of ZC and Ag⁰-ZC samples.

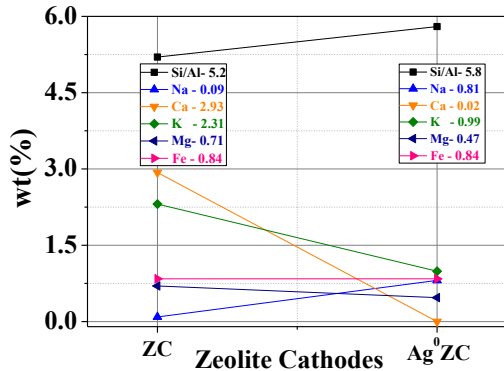


Fig. 1. The SEM-EDX determined chemical composition of unmodified and Ag⁰-ZC samples.

The experiments were carried out with natural ZC and silver modified Ag⁰-ZC plate ($\rho \sim 10^{11}-10^6 \Omega.cm$) [9]. The ZC used in this work is plates having a diameter D of 22 mm and a thickness of 2 mm. The pressure in the chamber was monitored by a digital manometer attached to a pumping system and was kept at a certain constant value during the whole course of measurement. The entire experimental study of this work was performed in ambient air from AP to 10^{-2} Torr pressures and the

measurements were carried out at room temperature. The setup (Fig. 2) used here is similar to that applied earlier [10,11], where a GDED with a GaAs photodetector was studied at room temperature.

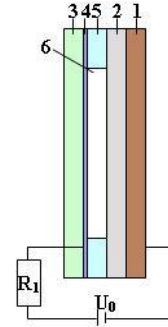


Fig. 2. Scheme of the gas discharge cell: 1- metallic contact; 2- zeolite plate; 3- flat glass disk; 4- semi-transparent conductive SnO₂ contact; 5- insulating mica sheet; 6- gas discharge gap.

3. RESULTS AND DISCUSSION

I-V characteristics of a GDED with ZC and Ag⁰-ZC for different pressures were investigated. Fig. 3 gives typical I-V characteristics for the discharge cell with different gap distances d (50-250 μm) of the ZC. Due to the very small d we can describe the behaviour of the charged particles in the electric field of GDED with the dc Townsend break-down theory, depending on the pressure range. At this point, we assume that a homogeneous stationary Townsend discharge [12] is established in the GDED. From the physical point of view, the most important feature of this kind of gas discharge is that space charge effects inside the gap are small and do not cause a distortion in the electric field between the electrodes. Another characteristic property is the homogeneous distribution of the current density perpendicular to the current flow. The DLE from the discharge is also homogeneous, while the wavelength of the DLE depends on the filled gas. The DLE intensity is proportional to discharge current. A local change of a ZC resistance leads to a local change of the current and the DLE [13].

Hence, the principle of operation of the GDED is based on some specific properties of the Townsend discharge. The voltage drop at the discharge gap for Townsend discharge mode is independent of the current. Therefore, the slope of the I-V characteristics provides the resistance of the ZC. Then, the specific conductivity can be computed from the resistance and the geometric dimensions. We notice that the current density in the GDED in the investigated parameter range does not exceed the limiting current for the existence of the Townsend discharge at given experimental conditions [14]. We remark that the feeding voltage V_0 is the sum of the voltage drops at the gas gap and at the zeolite component. One of the characteristic features of the Townsend discharge is the constancy of the voltage drop V_B at the discharge domain while current varies.

The range of the stationary operation and current depends on type of the ZC and interelectrode distances d [15]. Considering this figure for the GDED with a ZC and Ag⁰-ZC one can note the following: (a) the increment of

pressure leads to an increase in U_B values for air (i.e. at 44 Torr $U_B = 365$ V for ZC and $U_B = 345$ V for Ag^0 -ZC); (b) the current and U_B values rise abruptly at AP (i.e. at 760 Torr $U_B = 710$ V for ZC and $U_B = 380$ V for Ag^0 -ZC); (c) the high current values were obtained at lower voltages for Ag^0 -ZC compared to ZC electrodes. The slope of Ag^0 -ZC is higher with respect to un-modified ZC for a wide pressure range, which suggests that Ag modification (Ag^0 -ZC) leads to enhanced conductivity with respect to ZC.

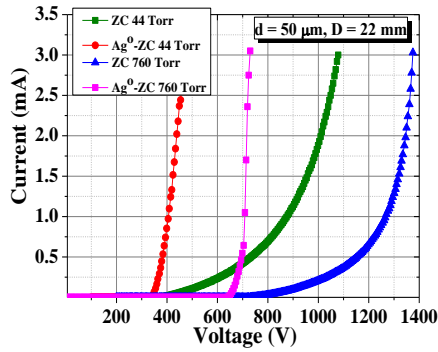


Fig. 3. I-V characteristics of a GDED with respect to pressure for ZC and for Ag^0 -ZC.

It can be seen that the I-V characteristics have a smooth current increase, but they are completely different from the same characteristics of the GDED with GaAs semiconductor cathode (for comparison see Fig. 2 in [16]). Fig. 3 also shows that with a change in type of ZC the U_B changes and the form of the I-V characteristics is reproducible, except for minor differences in the values of the current. Our previous works [17] commented on the physical properties of discharges generated inside the porous ZC by dc driven discharges. The detailed description of the discharge properties with respect to the effect of the pore size, discharge power, and gas mixture can be found in [18]. The results showed that the microplasmas inside the ceramic foam formed only for the specific discharge power and pores size of the ceramics. At small voltages, a surface barrier discharge on the surface of the ceramics may only be observed. With the increase of the applied voltage, however, the surface discharges transition into capillary microdischarges inside the ceramics, which onset voltage increases with the decreasing pores size. Upon the transition to microdischarges, the amplitude of the current pulses increases extremely, as well as the corresponding discharge current and power. The increase of the discharge current is larger for the bigger pore size, due to the increase of the radius of the discharge channel and volume of the generated microplasma.

Moreover, the adsorption of water by zeolites has some peculiarities. For all types of the zeolites very sharp rise of the isotherms is observed at low concentrations of water vapor. Adsorption capacity of zeolites at ambient temperatures (T_a) and for pressure of 1 - 2 Torr is very close to the maximum saturation P_w . Moreover, even at very low pressures NaA zeolite exhibits significant adsorption capacity of water [19]. The second

distinguishing feature of the water vapor adsorption by zeolites is to maintain the adsorption capacity even at significant change of temperatures. At $T_a = 100$ °C and $P_s = 10$ Torr, the adsorption capacity X of the zeolite is 15-16 g/100 g. Moreover, approach to 200 °C the X is still significant and no less than - 4 g/100 g [20]. With increasing T_a , the difference in the adsorption capacity X of zeolites is further increased, which is a distinctive feature of adsorption on zeolites. Oscillations of gas temperature do not introduce significant changes in the X of the synthetic zeolite. However, it should be noted the following significant disadvantage. Zeolites greedily absorb humidity, but they are hard to give it during dehydration process. At the same time, according to a global model based on He/ H₂O plasma chemistry, water vapor plasmas are dominated by OH, O, and O₂ metastable species and water cluster ions depending on the concentration of water vapor in the gas [21]. An increase in water vapor concentration in the gas mixture leads to an increase in the reduced electric field strength E/N in the plasma, which results in a higher intensity of OH generations [22,23]. Water is also an important impurity in numerous AP discharges of practical interest. For example, discharges in atmospheric air typically contain water vapour in concentrations of thousands of parts per million (air at 25° and 25% relative humidity contains ~ 7750 ppm of water) [21,24].

Strictly speaking, the most suitable interelectrode distance is $d = 50$ μm up to the AP. This situation indicates that the better stabilization of dc glow discharges at AP can be obtained for ZC in GDED. Thus, it is possible to produce gas discharges up to AP by means of GDED at moderate voltages so that wide areas of plasma applications become feasible under those conditions. For further step, the physical processes determining the stable function of an ionization system and spatial stabilization of the discharge can be taken into account as a result of the distributed resistance of the ZC. Because, stabilization effect is closely related to the I-V characteristics results obtained for different gap distances d in the discharge cell. Therefore, representative plots of measured breakdown curves for the ZC and Ag^0 -ZC in cases of different gap distances d are shown in Fig. 4.

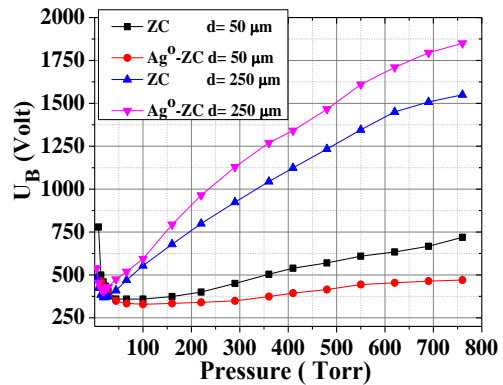


Fig. 4. Measured breakdown curves for the ZC and Ag^0 -ZC.

With a change in the residual gas pressure up to AP the current changes. In a running experiment, the pressure

p and the conductivity of the porous ZC and Ag^0 -ZC are fixed, and the supply voltage U_0 is slowly increased from 0 V, thereby increasing the voltage drop at the gas layer. As soon as U_0 reaches the critical voltage for breakdown in the gas, homogeneous ignition of the discharge takes place. The value of the critical voltage and residual pressure are determined by the so-called Paschen curve [25].

Inset in Fig. 5 shows detailed information regarding the I-V characteristics of the cell with respect to pressure when a dc voltage of a high enough magnitude is applied to the system. The voltage value from U_B to feeding voltage U_0 applied to the electrodes is the potential drop across the ZC, whereas the value from 0 to U_B is mainly the potential drop at the discharge gap. The optimal operation value of d is found as 50 μm for air-filled GDED. However, the atmospheric pressure is much more compatible and optimal for planar gas discharge cell with ZC, as shown in the values of current (see inset) and GDLE in Figs.5, respectively. In addition, discharge currents and GDLE intensities in GDED with Ag^0 -ZC at minimum feeding voltage (450 V) are much larger and intensive compared to the air-filled cell with ZC. In the GDED with ZC, GDLE satisfies the optimal and effective conditions at lower pressures (44-160 Torr), i.e., the current and DLE intensities in this media are high. However, the situation of current and GDLE intensities becomes vice versa near the AP. In other words, while an instant decrease in the GDLE intensities from the GDED with ZC is observed, higher GDLE intensities are obtained from cell with Ag^0 -ZC, conversely. Moreover, maximum GDLE intensity values are very different in GDED with ZC, whereas these values are the almost the same in system with Ag^0 -ZC near the AP, as shown Fig. 5. This situation proves that one should prefer to use Ag^0 -ZC at APs rather than ZC since the GDLE values are considerably better. It can be also stated that the better stabilization of dc glow discharges at APs can be obtained for GDED with Ag^0 -ZC.

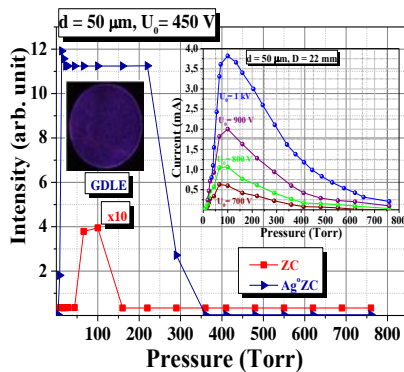


Fig. 5. GDLE dependence on pressure for GDED with ZC and Ag^0 -ZC.

It is also found that the slopes of current curves depend on the D . GDLE inside the porous zeolites develop from the surface if the amplitude of the applied voltage reaches given threshold. Discharge inside the pores of ZC framework is produced by dc power supply and produce relatively cold microplasmas with high level

of non-equilibrium with no instabilities. It is found that the gas in ZC pores ionizes and, accordingly, the number of electrons in the pores grows. It is shown that especially Ag^0 -ZC in a planar gas discharge cell considerably reduces the ignition voltage of the GDED.

Fig. 5 shows the same behaviour of the GDLE in a gas discharge cell with the Ag^0 -ZC and ZC. For a thin discharge gap of the cell the proportionality between the gas brightness and the current density, j , can be observed in a broad range of j . Note that when the feeding voltage is higher than 400 V, the curve for Ag^0 -ZC in Fig.5 represents the saturation of the GDLE intensity, which is related to the maximal limit of the photomultiplier. Moreover, the shape of the I-V characteristics and the GDLE intensity in a system depend on the voltage increment of the power supply [10].

The dependence of the intensity of the GDLE and ignition of discharges associated with all nanopores of ZC on the electric field strength is shown in Fig. 5. We have observed a significant increase of the discharge brightness in the discharge gap with Ag^0 -ZC compared to that of the main traditional discharge gap with unmodified ZC [26]. It is seen that the gain G increases exponentially with feeding voltage. Such dependence is in accordance with the literature data for gain measurements in gas electron multipliers [27] and reflects the existence of the avalanche electron multiplication mechanism. One can see that in this case there is a significant increase in the output brightness, which takes place thanks to initiation of a self-sustained discharge in the multichannels. At fixed feeding voltage U_0 the brightness is proportional to the current density of the gap and seems to behave linearly to the current range covered here. The maximum gain achieved in the present work is 50 for the pressure of 100 Torr and the feeding voltage $U_0 = 450$ V. The filamentation was primarily due to the formation of a space charge of positive ions in the discharge gap, which changed the discharge from the Townsend to the glow type [28,29]. The intensity of GDLE in the system with Ag^0 -ZC exceeds the intensity of the DLE in the system with ZC.

The obtained electrical characteristics of GDED with a Ag^0 -ZC and the comparison of the discharge patterns show that the system possesses a noticeably larger discharge light amplification or gain G . Electrons entering the pores of the Ag^0 -ZC in the discharge gap are multiplied in the electric field by the avalanche mechanism, so that a rather small current in the discharge gap without pores becomes a much larger current in the gap with Ag^0 -ZC. Since the current is concentrated in the pores of ZC, the source of the loss of resolution i.e., electron scattering with the flight between the discharge electrodes disappears [30]. Thus, the GDED with ZC and Ag^0 -ZC shows good technical performance. The GDLE of the latter is observed from the backside of the structure. Thus, it is experimentally demonstrated that gas discharge gap with ZC can be used for generating and sustaining a stable, uniform and homogeneous non-thermal atmospheric pressure plasma.

4. CONCLUSION

In this study, we showed that Ag-modified-zeolite is an effective material for reducing the breakdown voltage

(U_B) substantially and charge transport occurs at lower voltages with respect to un-modified zeolite. Moreover, some new results were related with the role of Ag metal NPs in the discharge characteristics, including the analysis of physical processes initiating the electrical breakdown and spatial stabilization of the current in order to enhance electro-chemical/ electron-transfer processes and maintenance of stable discharges up to AP.

By analysing the current and optical emission from a plasma discharge, more complete information can be obtained about the possibility of varying the intensity of the light emitted by a *GDED* with ZC, especially with its working as plasma light source with the prolonged working time. Specific geometry of the zeolite channels structure and the strong electric field in the nanopores provide an efficient electron multiplication and related excitation of gas atoms. The use of gas discharge gap with nanoporous Ag^0 -ZC leads to increase in the *GDLE* intensity. In a system with Ag^0 -ZC, the total intensity of *GDLE* exceeds the intensity of uniform *GDLE* in the *GDED* with ZC. This device may find an application in

for generating and sustaining a stable, uniform and homogeneous non-thermal atmospheric pressure plasma.

Thus, it is experimentally demonstrated that *GDED* with Ag^0 -ZC can operate as an effective light intensifier up to AP with gain values of 40÷50 observed. We also believe that on the basis of the outlined principles, by using dielectric spacer of proper design with a large number of multi-channels and a single-hole microcapillary discharge plate (i.e. suggested in [31]) it is possible to build ultrafast and rather sensitive large emitting area plasma light source with internal image amplification.

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