



Effects of pressure and electric field on the charge transport mechanisms in the silver-modified-zeolite porous microstructure



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ARTICLE INFO

Article history:

Received 4 August 2015

Received in revised form

7 October 2015

Accepted 19 October 2015

Available online 27 October 2015

Keywords:

Atmospheric pressure

Charge transport mechanisms

dc conductivity

Electrical properties

Silver modified zeolite cathode

ABSTRACT

The electrical properties and charge transport mechanisms for nanoporous natural zeolite of clinoptilolite and its silver modified form were studied for the first time in a wide gas pressure range (4–760 Torr) and electric field strength (50–350 kV/cm) at room temperature using two different cell configurations. One of the used cells contained a gas discharge gap, which allowed investigating the electronic conduction route in zeolite cathodes (ZC) as well. The influence of pressure, electric field and cell types on the dc conductivity was described. The resistivity decreased intensely from 10^{10} to $10^6 \Omega \text{ cm}$ at 435 V upon increasing the pressure from 4 to 760 (AP) Torr, which can be due to the ionic mobility of ZC. The physical role of Ag metal nanoparticles in the generation and maintenance of cold plasma stabilization over the surface of ZCs was investigated. For this purpose, the effect of pressure and electric field on the charge transport mechanisms in the silver-modified-zeolite porous microstructure and physicochemical interaction of the discharge plasma with the different Ag loadings as was studied. The electric field and pressure was found to be basic parameters determining the characteristics of the discharge plasma and charge transport mechanisms. When high voltages were applied to the cell with gas discharge gap, the ionization phenomena was observed to increase, which indicated that the electronic conduction is most likely to contribute to the dc conduction in the zeolite. Therefore, the ionic and electronic transport mechanisms were both found to influence the transport mechanisms.

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1. Introduction

Atmospheric pressure (AP) glow discharges are attractive for a wide range of material processing applications mostly due to their operation flexibility afforded by the removal of the expensive vacuum system. At AP, reaction rates are higher [1] due to the high density of species. The high density of species thereby increases the collision frequency in AP plasma [2] compared to its low-pressure counterpart. The formation of spatially uniform, non-equilibrium AP plasma discharges [3] is desirable due to their potential industrial applications [4], such as deposition and etching used in the semiconductor manufacturing industry, pollution control [5],

ozone synthesis [6], surface treatment [7] and light sources with emission over a wide spectral range from deep UV to IR. Experimental studies are performed to use the micro glow discharge for plasma light source. Even though the substantial amount of progress made in both theoretical and experimental studies of plasma, there has been intense interest in the scientific community to develop and implement non-thermal plasma in a variety of different venues before practical use in industry. However, lack of preliminary studies requires further detailed study of the physical and physicochemical properties in plasma science and to clarify the possibilities of using nanoporous materials, such as zeolites, for practical usage in plasma applications. The gas discharge electronic devices (GDEDs) with a semiconducting photocathode have used for various necessities in the IR image converter [8] and alternative large emitting area UV plasma source [9]. Therefore the interaction of non-thermal plasma with nanoporous surface is currently of great interest as a possible solution for those deficiencies and to

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manifest further optimization of the GDED. Recently, physical interactions between nonthermal plasma and metal nanoparticles supported on various zeolites (such as MS-13X, mordenite) had been reported [10], which showed that zeolite supported metal nanoparticles assisted discharge plasma to expand over a wide surface area. Experimental data is needed to provide insight into the physicochemical processes that affect the plasma characteristics and hence plate properties.

Nanoporous zeolites have three-dimensional framework structures. The zeolite structure is built from TO_4 ($T = Si, Al$) tetrahedra which are linked together to form a three-dimensional framework of interconnecting pore and channel structure. The conductivity of zeolites is usually associated with ionic conductivity [11,12]. Charge is carried by means of the motion of mobile charge balancing ions in the anion framework. Hydrated zeolites are also known as proton conductors and hydroxyl ion conductors [13]. It is usually presumed that zeolites do not act as electronic conductors [14]. Furthermore, dielectric materials such as zeolites have the ability to store energy upon the application of external electric field [15]. Specific electronic properties of nanopores in zeolite structure make zeolites good candidate materials in the electronic industry, so that silicon-based technologies could be replaced or supplemented by nanoporous zeolitic materials. The possible applications of zeolite materials range from microelectronics [16], gas sensors [16], solar cells [17], functional fillers in composites [18], and low power consumption for building a plasma light source [19].

In the current study, the effect of electric field and pressure on charge transport mechanisms and dc conductivity of silver-modified zeolite microstructure is presented. For that purpose, clinoptilolite with high Si/Al ratio, which is one of the most commonly found natural zeolite type, was studied as an electrode material, which normally has large applications in industry and agriculture. Its electrical properties have always been of interest, with special emphasis on ionic conductivity due to mobile cations that are readily found in zeolitic channels. This mobility is known to be effected by guest molecules, where the zeolite matrix is stabilized by inclusion of metallic clusters. It would have been of special interest to be able to tune the electrical properties of these nanoporous materials by controlled environment (i.e., pressure, electrical field, Ag nanoparticles, etc.) as well as inserting guest molecules. Silver modification of zeolites has always been of interest for tailoring the already existing antibacterial, chemical, optical, and electronic properties of zeolites [20,21].

Up to now, the structure and chemical composition of zeolite materials have been studied adequately, but there is insufficient knowledge about the physical properties associated with transport phenomena. These studies were predominantly investigated at ambient pressure as a function of temperature [22] with only very limited studies at high pressure and room temperature [23]. Our earlier study [9] indicated that GDED with semiconductor cathode (i.e., GaAs cathode) cannot operate efficiently at AP in air media, where as using natural zeolites as a cathode material makes this operation possible [24].

Accordingly, the main goal of this work is to achieve the idealized dc conductivity measures using a nanoporous medium, especially at AP for future microelectro-optic applications [25]. For this purpose, the charge transport behavior of silver nanoparticle doped zeolite cathode (Ag^0 -ZC) and the changes induced upon ionic/electronic transport within the zeolitic medium (i.e. new mixed transport mechanisms-electronic and ionic-of aluminosilicate materials) was investigated profoundly. This behavior was studied at AP and compared with results obtained at low pressure. Furthermore, the effect of changing the applied voltage as well as constant electric field using two different cell designs was realized, which allowed to interpret the electronic as opposed to ionic

transport behavior in Ag^0 -ZCs. This allowed us to investigate the, bulk electrical conductivity of Ag^0 -ZC to understand the entire conduction mechanism that is required to ensure proper optimization of GDED. Consequently, the occurrence of discharge plasma in the GDED system was shown for the first time, which was mostly influenced by the increased amount of Ag metal nanoparticles. Therefore, in this study we investigate the enhanced efficiency of Ag^0 -ZC on the fundamental characteristics of GDED.

Besides operation at AP, in this study we showed that silver-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 nanoparticles in the discharge characteristics, including the analysis of physical processes initiating the electrical breakdown and spatial stabilization of the current in order to enhance electrochemical/electron-transfer processes and maintenance of stable discharges up to AP. To our knowledge, this is the first study, which has been undertaken to better understand the effect of physicochemical interaction with the discharge plasma and operating parameters on the nonthermal plasma generation and operation of such stable discharges up to AP.

2. Experimental

2.1. Silver modification of zeolite cathodes

The samples for ZC were obtained from Gördes Manisa, which is located in the Western part of Turkey. The un-modified disk-shaped clinoptilolite plates were purchased from a Turkish mining company, Rota Madencilik A.S. The chemical formula of the used clinoptilolite is $(Ca, K_2, Na_2, Mg)_4Al_8Si_{40}O_{96} \cdot 24H_2O$ with the chemical 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%, SiO_2/Al_2O_3 5.4–7.2%. The ZC used in the cells during experiments was manufactured from ZC by cutting and giving the expected shape of ZC with a diameter (D) of 22 mm and a thickness of 2 mm. The benefit of such a manufacturing process has several advantages, such as a very compact design of cathode material as opposed to using zeolite in its original powder form and avoiding the very common use of binders. The un-modified zeolite cathodes were denoted as ZC.

Three types of silver modified clinoptilolite samples were prepared. In the first one the purchased bare clinoptilolite samples were silver ion-exchanged by using silver nitrate ($AgNO_3$) solution and silver ions (Ag^+) were reduced to silver nanoparticles (Ag^0) by using sodium borohydride ($NaBH_4$) solution. In the preparation method, the clinoptilolite plates were immersed into 0.020 M silver nitrate ($AgNO_3$) solution and stirred for 24 h at room temperature, then rinsed with deionized water and dried at 55 °C oven for overnight to prepare silver ion-exchanged form of $Ag(0)$ -ZC-I samples. For chemical reduction of silver ions to silver nanoparticles 0.1 M sodium borohydride ($NaBH_4$) solutions were prepared. The silver ion-exchanged clinoptilolite plates were immersed to $NaBH_4$ solution for 40 s, and then rinsed with 1 L deionized water and dried at 55 °C oven for overnight. The first silver nanoparticle incorporated sample was denoted as $Ag(0)$ -ZC-I. In the second sample, the goal was to increase the Na content of the original sample, since Na is the most easily exchanged cation with Ag. For that purpose, original plates containing Ca^{2+} , Fe^{3+} and K^+ ions were initially sodium ion-exchanged using 0.1 M NaCl solution and stirred for 24 h at room temperature in closed beaker. These clinoptilolite plates that were Na^+ -ion-exchanged were immersed into 0.020 M $AgNO_3$ solution and stirred for 24 h at room temperature, then rinsed with deionized water and dried at 55 °C oven

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