

EXPERIMENTAL EVIDENCE FOR CHEMO-ELECTRONIC CONVERSION OF WATER ADSORPTION ON THE SURFACE OF NANOSIZED YTTRIA-STABILIZED ZIRCONIA

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Direct energy conversion techniques are now dominated by photovoltaics. But, this dominance will be soon challenged by the emergence of a new conversion methods, known as so called “chemovoltaic”. Here we demonstrate the possibility of the electric energy generation through interactions of atmospheric moisture and ZrO₂ based nano-

powder systems. Such electric energy generation occurs by the conversion of the energy of exothermic heterophase electrochemical reaction. Creation of electromotive force is confirmed by electrical measurements of experimental specimens at a saturation flux density gradient of atmospheric moisture.

1. Introduction

Creation of novel alternative energy generation processes is of major importance in nowadays conditions of extreme electricity consumption [1]. Water is the one of the main conventional sources of alternative energy used by mankind. In its liquid phase is traditionally used for the kinetic into electric energy conversion by so-called hydropower plants. In 2016 by hydropower was generated 16.7% of the world's total electricity and around 70% of all produced renewable electricity [2].

However, direct conversion of water molecule energy into electricity remained unrealizable for centuries as a top scientific and practical aim.

The pioneer of the experiments on capturing electricity from the air was Nikola Tesla (1932). Since the beginning of the 21st century [3, 4], the hypothesis of Nikola Tesla [5] to use atmospheric energy (humidity, as founded later) as a renewable energy source, started to be explored by the scientific community. However, these developments are on their infancy [6, 7].

With the development of nanotechnology, the implementation of these ideas become potentially possible. Nowadays it is known that gas adsorption (including water vapour) can generate electric charges on metal surface [8]. Due to the interaction of gas molecule with metal film of nanometer thickness < 10 nm the so-called "hot electrons" can occur and ballistically i. e., without the loss of energy reach a Schottky barrier, cross it through kinetic energy, and by entering into the semiconductor material create an electric current in the external chain. However, efficiency of the such conversion method is limited by a low number of generated "hot" electrons (10^{-3} – 10^{-5}) per interaction act. Moreover, a small cross-section of free charge carriers in semiconductor crystals leads to a conversion efficiency decrease. Thus, the electric field (of heterojunction) decays drastically with an increase of the distance from the surface even for a few interatomic distances, therefore, only a small fraction of gas can act effectively at the heterophase process on the "front" surface of a semiconductor crystal. From this aspect is of high interest to use dielectric materials with developed surface area. We expect the electrostatic field of dielectric materials significantly exceeds the electric field of heterojunction and consequently leads to an increase of conversion efficiency.

In the present work, we show experimental verification of water induced electromotive force (EMF) generation through adsorption on the surface of nanosized yttria-stabilized zirconia (YSZ, $\text{ZrO}_2+3\text{mol}\%\text{Y}_2\text{O}_3$).

2. Experimental Section

2.1. Specimens preparation

The compact (compressed) structures of tetragonal polycrystalline zirconia (TPZ) ($\text{ZrO}_2+3\text{mol}\%\text{Y}_2\text{O}_3$) nanopowder of a particle size between 9–12 nm were used (Fig. 1). Detailed description of nanopowder production can be found elsewhere [9]. However, the general steps of technological operations are the following. At first, zirconia hydroxide is produced by co-precipitation method from the chloride raw materials. After 0.4 h of dehydration in microwave oven at 120 °C, amorphous nanopowder was crystallized through annealing at 400 °C for 2 h.

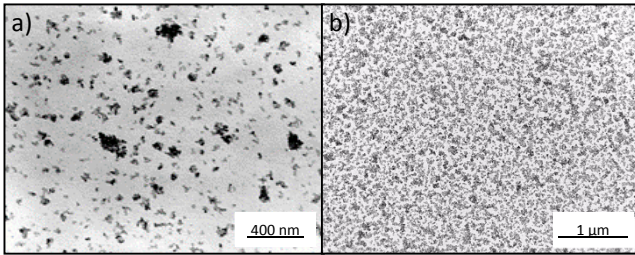


Fig. 1. TEM images of produced TPZ nanopowder annealed for 2 h at 400 °C, at different magnification a) 400 nm and b) 1 μm .

Compact specimens were obtained by compression of 1 g of TPZ nanopowder using uniaxial pressure of 40 MPa until the tablets of 20 mm in diameter and of 2–3 mm height were formed. For the final formation after the compression tablets were pressed by a high hydrostatic pressure (HHP 500 MPa). Then graphite electrodes were deposited mechanically on the sides of the tablets (Fig. 2).

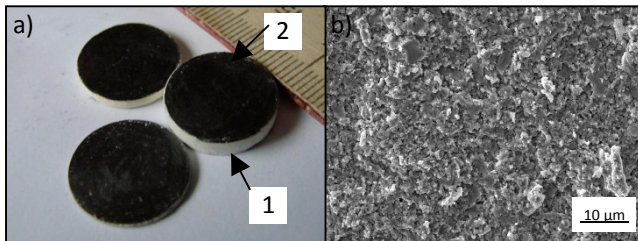


Fig. 2. TEM images of produced TPZ nanopowder annealed for 2h at 400 °C, at different magnification a) 400 nm and b) 1 μm .

1.2. Specimens characterization

The spatial and structural formation of the samples was investigated by transmission (TEM) by using the procedure described elsewhere [10] and scanning (SEM) electron microscopies using JEM 200A and JSM640LV (JEOL) instruments respectively.

The EMF measurements and sample humidification were performed in a static mode at fixed values of relative humidity (RH, 75%), barometric pressure (760 mmHg) and temperature (19 °C).

Saturation of the specimens by humidity within time was measured gravimetrically using the Moisture Balances ADGS50 and calculated by the following formula: $\Delta m = f(t)$, where $\Delta m = (m - m_0)/m$, m_0 is the mass of the dehydrated tablet at the beginning of the measurement, m is the mass of the hydrated tablet.

The EMF measurements were held under the same humidity/temperature/pressure conditions. Measurements of the potential difference across the electrodes ($V = f(t)$) of table specimens were carried out by the voltmeter JT-87 at load (R_L) of 1 MOhm. Voltage points were taken with an interval of 10 min for 2 h.

Prior to the experiment one end side of the tablet was covered by a waterproofing layer of paraffin in order to create a gradient water adsorption thus, allowing for movement of generated charge carries.

It should be noted that all measurements were repeated 3 times and estimated standard deviation values did not exceed 3%.

3. Results and Discussions

The typical SEM image of the tablet cross-section is shown on Fig. 2b. As can be seen the microstructure of tablet is relatively friable. The calculated density of the tables is about 3.1 g/cm³, which corresponds to about 40–50% from the density of the typical ZrO₂-based ceramics. Moreover, the branched network of relatively large (about 1 μm) pores is present in the bulk of specimens. Thus,

water can easily get into the bulk of a tablet. Most probably, at first water molecules draw into the pores of large size and then fill with the slower rate the remaining volume of the material spreading through smaller pores. As can be seen from the gravimetric curve (Fig. 3, circles) the amount of adsorbed moisture increases monotonically with time, until reaching a constant plateau. After 100 min, the saturation occurs where the weight of the tablet remains unchanged. The change of the specimen weight at saturation corresponded to the adsorption of 4 wt% of moisture. From the curves represented in Fig. 3 the correspondence between the specimen saturation dynamics (circles) and its electrical properties (squares) can be established.

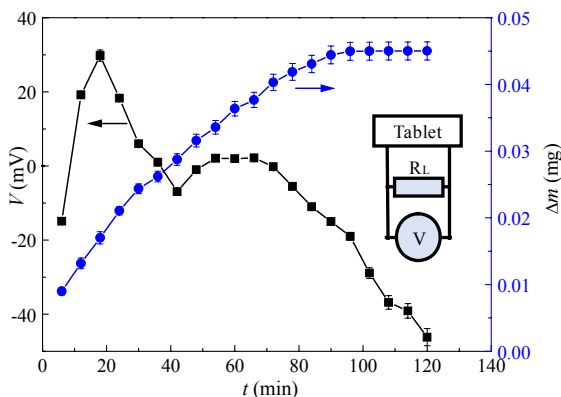


Fig. 3. Variation of weight, Δm (circles) and the EMF, V (squares) of the tablet specimen within saturation at 75% of RH. An inset represent EMF measurement circuit at load (R_L) of 1 MOhm. The lines are given as guide for an eye.

Herewith after 20 min (the first stage) the potential difference between the electrodes $V(t)$ increases up to 60 mV (Fig. 3 squares). The dependence of $V(t)$ in contrast to the dependence of $\Delta m(t)$ is not monotonic and during the following 20 min (the second stage) the potential difference between the electrodes decreases and the polarity of voltage gets inversed (the third stage). The amplitude of the signal of the reverse polarity is approximately 25% from the total EMF amplitude. According to the form of the EMF curve, it can be concluded that the electrochemical process in the sample material has two steps. Initially, the electrodes were separated by an insulating layer of a dehydrated specimen material and have fixed potentials. A slight potential difference (-20 mV) observed at the beginning of the measurements ($t=0$ min) might be induced by polarization of the sample during the compaction process (electrets effect [11]). During humidification, the potential of the water permeable electrode increases because of localization in a bulk of the adjacent space region of generated free

charge carriers through the nonequilibrium chemoelectronic process (the first step) [8], while the electrical resistance of the layer between electrodes is still large (about 10^6 – 10^7 Ohm/mm) in accordance with impedance spectroscopy (not shown here). While, the potential of the waterproofed electrode remained constant. Within moisture distribution through the pores of the tablet and adsorption in the bulk, the potential equalization and the appearance of bulk conduction current occurs (the second step). The bending of the potential curve is observed after 40 min of measurements. As can be seen the increase in the amplitude of the EMF and its reduction occurs at a constant rate of tabled saturation (an unchanged slope of the curve). Consequently, the inversion of the sign of the derivative $V(t)$ over the time happened not due to the change of nature of the mass transfer process, but rather, due to the specimen geometry.

4. Conclusions

We show a possibility of the electric energy generation through conversion of moisture adsorption energy on the surface of ZrO_2 based nanopowder systems into electrical charges. Such chemoelectronic coupling can be a base for novel methods of sensing, in which the sensor is based on active charge carrier production rather than on passive variations in equilibrium thermodynamic quantities, such as resistivity or capacitance-based devices or at the appropriate level of development be a novel energy conversion device “chemovoltaic”. Maximum power density produced by investigated tablets was estimated around 10 nW/cm^2 .

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