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Nonequilibrium chemo-electronic conversion of water on the nanosized YSZ: experiment and Molecular Dynamics modelling problem formulation

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Abstract. The exothermic heterogeneous electrochemical energy conversion to the electric energy through interaction of the ZrO₂-based nanopowder system with atmospheric moisture was explored within this work. Electrical properties of the experimental samples were investigated during humidification at the conditions of molecular flux density gradient. The morphological features of the surface cross-section and aggregates of 3 mol% Y₂O₃-doped ZrO₂ nanopowder systems were investigated. Initial conditions for molecular dynamics modelling of the adsorption processes were obtained. A novel approach for developing of chemo-electronic converters based on nanoscale processes and materials with dielectric conductivity type proposed.
1. Introduction
Development of a new electricity generation techniques is one of the most relevant tasks, especially nowadays under conditions of extreme growth in energy consumption [1 - 2]. The water is well known conventional source of electrical energy used by mankind. In liquid state, it is traditionally used for the electric energy conversion by an external thermostat of hydropower plants. However, direct conversion of water in gas state, (atmospheric moisture) to electric energy, remained unrealizable for centuries as a top scientific and practical aim. With the development of nanotechnology, the implementation of these ideas become potentially possible. In this regard with nanopowder system based on ZrO₂ is the best candidate for the direct conversion of the energy of water adsorption into electric energy.

It is known [3] that extremely nonequilibrium thermodynamically, the surface of nano-dispersed oxide systems is exist in a state of dynamic charge and adsorption equilibration. I.e., the change of quantity of adsorbates is accompanied by a changing of the total charge in the system. In the case of nanoscale powder of zirconia dioxide, on its surface are preferably water is adsorbed, and certain stages of a matter exchange between the system and external environment have an exothermic behaviour. Hence, in a cyclic mode, the nanopowder system based on ZrO₂ can convert the chemical energy of water molecules adsorption to an electric form. The possibility of such processes has been shown previously for the bulk semiconductors [4 - 5].

The aim of present work is the experimental proof of concept and formulation of a problem for the following Molecular Dynamic (MD) calculations of water adsorption on the surface of nanosized yttria-stabilized zirconia (YSZ).

2. Experimental section
2.1. Specimens preparation.
As an object of study the compacts (compressed structures) of YSZ (ZrO₂ + 3 mol% Y₂O₃) nanopowder with a particle size 9 nm were used (Figure 1). As can be seen from Fig. 1, the nanoparticles are monodisperse and well distributed. Consequently, the binding of aggregates is weak and adhesion between particles of this powder is low. The technology of nanopowders production was previously published in [6] and contains several technological operations. At first, by co-precipitation method from the chloride raw materials the hydrated zirconia hydroxide was obtained. After dehydration in a specialized microwave oven (T = 120 °C, t = 0.4 h) an amorphous powder was crystallized through annealing at 400°C for 2h. Then, in order to create the compacts structures, 1g of obtained powder was compressed by uniaxial pressure of P = 40 MPa until the tablets of 20 mm in a diameter and a height of 2-3 mm were formed.

Figure 1. TEM image of ZrO₂+3mol% Y₂O₃ nanopowder prepared at, 400°C for 2h.
Before the compression in order to unify initial physical conditions the powder was pre-treated in an oven at $T = 120\, ^\circ\text{C}$ for 1h. After the tablets form creation, the specimens undergo compression by a high hydrostatic pressure (HHP, 500 MPa). Then, the graphite electrodes were deposited mechanically on the sides of the tablets (Fig. 2).

The pre-treatment of specimens before measurements consisted of dehydration through drying at 120 °C for 1h. After dehydration samples was placed in a climatic chamber under specific conditions of temperature $T = 21\, ^\circ\text{C}$ and relative humidity $\eta = 70\%$. It worth noting that prior to the placement of specimens into the climatic chamber the spherical clamping silver contacts were attached to the graphite electrodes. In order to create the potential difference between the contacts during the adsorption of water molecules a gradient of physical properties within the specimen was created. Thus, the adsorption at one side of the tablet has been limited by deposited waterproof layer of paraffin.

2.2 Samples characterization

The spatial and structural characterization of the samples was performed by transmission (TEM) [7] and scanning (SEM) electron microscopies using JEM 200A and JSM640LV (JEOL) instruments respectively.

![Figure 2. a) Specimen - tablets (1) with graphite electrodes (2) and b) electrical circuit of measurement, where $G$ – specimen in generation mode, $R$ – applied load (1MOhm), and $V$ - digital voltmeter.](image)

Small-angle neutron scattering (SANS) experiments were done using the time-off-light YuMO spectrometer and the IBR2 highflux pulsed reactor (Dubna, Russia). The detectors of the spectrometer were located at distances of 5.28 and 13.04 m from the sample; the range of transferred pulses $q$ attained in the experiment was from 0.006 to 0.5 A$^{-1}$ [8, 9]. X-ray diffraction analysis (XRD) of the samples was performed using an Empyrean diffractometer (PANalytical). Measurements of potential difference (EMF) of produced samples were carried out by digital voltmeter AM1199 (AKTACOM) under eclect circuit shown in Fig. 2b.

3. Results

3.1. Experimental realization of the chemoelectronic conversion effect.

The variation of changes of potential differences (EMF) and mass $\delta m$ of the specimen within the time is shown on Figure 3. As can be seen, the change of specimen mass increased monotonically, and reaches saturation plateau after 100 min. During this time, the sample adsorbs around 4 wt% of moisture. Herewith after 20 minutes the potential difference between the electrodes $V (t)$ increases up to 100 mV. The variation of $V (t)$ in contrast to variation of $\delta m (t)$ is not monotonic and during the next 80 minutes the potential difference between the electrodes is decreases and the polarity of voltage is inversed. The amplitude of signal of reverse polarity is approximately 25% from the total EMF amplitude. According to the form of the EMF curve (Figure 3), it can be concluded that the electrochemical process in the sample material has two stages. Initially, the electrodes are separated by
an insulating layer of dewatered samples material and have fixed potentials. A slight potential difference usually takes place even in the initial state. It is induced by polarization of the sample during compaction process (electrets effect [10]). In our case, such value is around 20 mV (Figure 3, curve 2). During the humidification process of specimen, the potential of water permeable electrode increases because of localization in a bulk of adjacent space region of a free charge carriers through nonequilibrium chemo-electronic process (First step) [11], wherein the electrical resistance of layer between electrodes is still large (according impedance spectroscopy of about $10^6 - 10^7$ Ohms / mm).

![Graph showing variation of weight and EMF over time.](image)

**Figure 3.** Variation of weight, $\delta m$ (1) and the EMF, $V$ (2) of the sample changes from the time.

The potential of waterproofed electrode remains constant. During the distribution of moisture within pores of the tablet conductivity between the electrodes begins increase whereas a potential difference between electrodes decreases accordingly (Second step). Increasing of the potential differences is observed at 20 min. There is an inflection on the potential curve herewith, as can be seen from curve 1, the dynamics of water absorption of tablet is monotonous. This indicates that the generation of power by tablet is limited exclusively by the geometric features of sample, rather than the nature of the mass transfer process. The nature of the minimum observed on curve 2 (Figure 3), occurred after 40 minute is not clear yet.

3.2. *Investigation of physical properties of the specimens. The morphology of the specimens.*

The typical SEM image of the tablet cross-section is shown on Figure 4.

![SEM image of tablet cross-section.](image)

**Figure 4.** SEM image of the tablet cross-section.
It can be seen that the microstructure is relatively friable. The calculated density of the table is about \( \rho_c = 3.1 \text{ g/cm}^3 \), which constitute about 40-50\% of the density of ZrO\textsubscript{2}-based ceramics. Moreover, the branched network of relatively large (approx. 1\( \mu \)m) pores is present in the bulk of specimen. Thus, water can easily seep into the bulk of tablet. Most probably, the first water molecules in the gas phase fill pores in the surface layers of tablet, and then, with a delay proportional to the resistance of the flow are penetrates to bulk.

3.3. The bulk structure of the samples. SANS - investigation.

The SANS spectra of tablets (curve 1) and nanopowder (curve 2) are presented in Figure 5.

![Figure 5](image)

**Figure 5.** The results of investigation of spatial structure of sample by SANS, where 1 - the scattering of the nanopowder ZrO\textsubscript{2} + 3 mol\% Y\textsubscript{2}O\textsubscript{3} with a particle size of 9 nm; 2 - scattering of the tablet and 3 - scattering of water; 4 - fitting curves.

To compare the amount of water in the samples, scattering from pure water is shown in Figure 5 (curve 3). The scattering was divided on two parts. Low \( Q < 0.03 \text{ A}^{-1} \) region was described by Guinier law and large \( Q > 0.03 \text{ A}^{-1} \) region was described by scattering from sphere:

\[
I(Q) = A \cdot \exp(-\frac{R_g^2 Q^2}{3}) \quad Q < 0.03 \text{A}^{-1}
\]
\[
I(Q) = B \cdot \left(3 \cdot \frac{\sin(QR) - QR \cos(QR)}{(QR)^3}\right)^2 + C \quad Q \geq 0.03 \text{A}^{-1}
\]

where: \( R \) is the radius of nanoparticles, \( A \) and \( B \) are scaling parameters and \( C \) – is the background constant, corresponding to incoherent scattering (the presence of H\textsubscript{2}O in system).

Guinier law allows to estimate aggregation number of nanoparticles, whereas large \( Q \) region gives the information about internal structure of system, in particular - the average size of particles. In both cases (nanopowders and tablets) the scattering is well described be spheres of diameter 9nm, whereas the aggregation for powders and tablets differs significantly and amounts to 15 and 5 nanoparticles, respectively. Thus, for the compressed structures the access of moisture to the surface of samples is available at all the scales.
3.4. Assumptions on localization and delivery mechanism of charge carriers to electrodes. Relationship between effects of chemo-electronic conversion and structural features of surface layer of nanoparticle.

Earlier V.I. Alekseenko et al [12] proposed an adsorption mechanism of Tetragonal - monoclinic transformation (T-M - transformation). Considering the T-M transition from the electrophysics standpoint, he revealed that a change in the charge state of the ion of stabilizer Y causes the T-M transformation in YSZ ceramics under chemical adsorption of H₂O. Ions of stabilizer exist in material in the form of impurity - vacancy dipoles (IVD) such as Y³⁺(+) - Vo⁻(>). In the solid solution, based of Zirconium oxide impurity atoms Y³⁺ have on the one electron less than Zr⁴⁺ atoms and they are acceptors. The impurity oxygen vacancies formed for compensation of excess of volume and charge of inovalent impurity - are donors. Vacancy Vo donates electron to Y³⁺ ion. Thus, a chemical bond between them is formed. The ionization energy of IVD is relatively small (E ~ 0,1 ÷ 0,6 eV) [13 -14].

A shift of electron density from the bulk of the adsorbate to adsorbates occurs during chemical interaction of adsorbate with surface of ZrO₂. The binding energy in IVD near the ZrO₂ particle surface decreases, hence its chain length Zr - Vo - Y, increases, which is accompanied by the transition in structure of the solid solution system with a large volume of cell - A phase. This effect on the surface of a bulk of ZrO₂-based ceramic was observed by the method of X-ray diffraction under the creation of high-stress concentrations using indentation [15]. After indentation in a thin layer of the ceramic material at the subsurface a 2-D monoclinic crystal was appeared. The T-M transformation in ZrO₂ – ceramic is reversible and has diffusionless mechanism, i.e., mutually convertible structures transforms into one another coherently, without breaking the bonds [16].

In nano-sized objects up to now the effect of changing of structure of surface layer of nanoparticles based on ZrO₂ was not discovered due to insufficient resolution of used research methods. However, considered effect of chemo-electronic conversion as one of specific manifestations of adsorption-induced electrokinetic processes suggest that recharging of ions of crystal lattice near the surface of nanoparticles is still going on. There is reason to think that an electric charge, localized from the crystal lattice of discussed structural transformation of adsorption type can be delivered by DEL – ions to the electrode in the presence of an external electric field or gradient of electrical properties of sample in the space between electrodes through the relay mechanism [17]. Specifically, due to a relay mechanism the hydronium and hydroxyl ions have higher numbers of charge transfer [18 - 19]. Limit of mobility of hydrogen and hydroxyl ions are 349.8 and 199.2 Sm•m² / mole, respectively and the mobility of other ions are in the range between 40 - 80 Sm•m² / mole. Proton hopping from hydronium ion H₃O⁺ to a certain way oriented neighboring water molecule is occurs during the relay mechanism. As a result, it becomes an H₂O⁺ - ion. Then proton is passed on to the next water molecules. These jumps occur much faster than the simple movement of hydronium ion, which provides high mobility and a high transport number of hydronium ion. Similarly explained the charge transfer of hydroxyl ions. In this case proton does hopping from water molecules to adjacent OH⁻ ions because proton in a molecule of water is linked stronger than hydronium ion, it jumps in this case more difficult, and the mobility of hydroxyl ion is lower than mobility of hydronium ions. At the moment from the available experimental data it is not clear what kind of ions is charge transfer with generalized heterophase boundaries on electrodes is carried out.

A charge transfer to an external electrical circuit occurs, consequently, as a result of ions discharge at the electrodes. The excess cations are then discharged at a cathode. Similarly, the anions are discharged at an anode, and its amount is thus decreases in its anode compartment. Thus, based on the nature of electrokinetic processes on the nanoparticles surface, we have to identify by MD simulations, the two main tasks (as were stated in part 1 of the Introduction):

(1) - to calculate the adsorption energy and to show the ability of nanoparticles surface ionization, i.e., an electron exemption from the volume of nanoparticles material into a dispersion medium during the water adsorption process;

(2) - to estimate a charge state of ions of ZrO₂ nanoparticles and to demonstrate the consequent changes of the crystal structure caused through the nanoparticles surface layers (T-M transformation).
3.5. Initial conditions for mathematical modeling of electrons generation in ZrO$_2$ based nanopowder system.

As initial conditions for the MD calculations of the ZrO$_2$+3mol% Y$_2$O$_3$ - nanoparticles material the structural parameters, obtained from the X-ray analysis data [20] were used. The X-ray pattern of investigated nanopowder sample of ZrO$_2$ + 3%Y$_2$O$_3$ is shown on Figure 6. According to the X-ray data, the material of the studied nanoparticles has a tetragonal type of crystal lattice P4$_2$/nmc. Calculated structural parameters of nanoparticle structures are shown in Table 1.

![X-ray pattern](image)

**Figure 6.** X-ray pattern of ZrO$_2$ + 3%Y$_2$O$_3$ - nanopowder sample.

**Table 1.** Atomic positions and isotropic thermal parameters of Zr$_{1-x}$Y$_x$O$_2$ (x = 0.05), calculated using Rietveld method from X-ray diffraction. P4$_2$/nmc: Zr (2a) (0.75, 0.25, 0.75); O (4d) (0.25, 0.25, z)

| Atomic parameter | x = 0.05 tetragonal P4$_2$/nmc |
|------------------|-------------------------------|
| a, Å             | 3.614 (2)                     |
| c, Å             | 5.167 (5)                     |
| V, Å$^3$         | 67.48 (8)                     |
| X                | 0.7500                        |
| Y                | 0.2500                        |
| Zr/Y             |                               |
| Z                | 0.2500                        |
| Biso (Å$^2$)     | 0.543                         |
| Occupancy        | 0.4735/0.026                  |
| O1               |                               |
| Z                | 0.04669                       |
| Biso (Å$^2$)     | 0.727                         |
| Occupancy        | 1.0                           |
3.6. Quantum molecular dynamics method of the adsorption processes on a nanopowders surface based on ZrO₂.
In the MD calculations the exchange-correlation potential approximation as generalized gradient approach formulated, by Perdew, Burke and Ernzerhof (GGA-PBE), and the effective potentials of ionic cores as projector-augmented plane-wave method seem to be a preferable approach. To describe the changes in the chemical bond energy, related to a hydrogen-producing process, a bond-overlap population analysis [21-22] and extended electron wave functions of the atomic orbital basis are of common method. So far, we do have a complete filling of the $Z_i(t)$ for the $i$th atom and the imposition of a set of links $O_{ij}(t)$ for a pair of $i^{th}$ and $j^{th}$ atoms, with dependence of time $t$. From $Z_i(t)$, to be easy estimate the charge of $O_{ij}(t)$ atoms, which can provide a semi-quantitative assessment of a covalent bond energy existing between the atoms. The nudged elastic band (NEB) method [23] and extend calculations to a free energy [24] of the assessment in the energy barrier in the chemical reactions and adsorption processes give us the general picture of the processes.

Method NEB provides the energy profiles of the processes at zero temperature. Calculation of free energy ensures to estimate the effect of the temperature on the outlined chemical reactions. Previously we have used a combination of these methods for the activation state calculations and estimation of the reaction parameters which are associated with the H₂O adsorption on a Al cluster surface [25 - 26].

4. Conclusions

1. It is shown that a nanopowder system based on ZrO₂ can convert chemical energy of gas phase water molecules adsorption to an electrical form. It was suggested that the mechanism of established effect is associated with chemical adsorption.

2. Experimental preparation and formulation of the problem for the molecular dynamics (MD) modelling of the moisture adsorption on ZrO₂ - nanopowder surfaces were made. The scientific and practical importance of the work lays down in new prospects for development of nonconventional ways for generation of electricity, in particular, direct conversion of gas-phase water adsorption energy to electric energy.

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