Chemical-Electric Energy Conversion Effect in Zirconia Nanopowder Systems

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Received October 11, 2016

Abstract—Issues concerned with the energy conversion of exothermal heterophase processes are discussed using the physico-chemical interaction between ZrO\textsubscript{2}–Y\textsubscript{2}O\textsubscript{3} (3 mol %) nanopowder system and atmospheric moisture as an example. The electrical properties of an experimental sample are investigated upon moisture saturation in the case of a molecular-flow density gradient. A probable mechanism for the effect based on the theory of contact phenomena in semiconductors is proposed. The idea of developing chemical-electric converters fabricated from nanoscale materials with dielectric conduction is suggested.

Keywords: nanoparticle, double electric layer, chemical-electric energy conversion, adsorption, new energy sources, size effects, nanoionics, electrokinetic processes

DOI: 10.1134/S1027451017030053

INTRODUCTION

The problem of new renewable energy sources is becoming more urgent as traditional energy sources are being depleted. The search for new methods of energy generation (transformation) continues. In this context, it is of interest to consider the ways of extracting energy released when heterogeneous electrochemical processes proceed with the participation of gas-phase molecules and active centers on solid surfaces.

There are several alternative techniques whereby a solid body converts extrinsic energy into electric current.

Semiconductor heterojunction. First of all, we deal with the use of photoelectronic and thermionic converters. The principle of their operation relies on the fact that an external electromagnetic field generates an electron–hole pair at the heterojunction between semiconductors with different types of conduction. To remove opposite charge carriers from a reaction cell, a heterojunction field whose amount is determined by the difference between the work functions of the contacting materials is employed. The charges are formed at the interface of macroscopic solid bodies with film structures.

Catalytic heterophase interaction. A more interesting case concerns functional heterojunctions between media with different aggregate states, e.g., between a solid body and a gas phase. Such heterojunctions also employ external radiation energy to create electron–hole pairs, but, as a rule, the outcome is a specific electrochemical process implemented on the surface of the solid-state (semiconductor) part of the junction, which is accompanied by the fact that the gas phase reagents traps the electron charge generated in the semiconductor. A widespread phenomenon of the given kind is photolysis, which is the key reaction observed in the formation of tropospheric ozone, namely, NO\textsubscript{2} + h\nu \rightarrow NO + O, and is also used in film photography (photolysis of silver halides). So-called “self-cleaning glasses” are finding application in construction, and antibacterial gas-flow facilities based on the photolysis of organic compounds (bacteria and fungus spores) are commonly used at home. These processes are attractive because their “hard” struc-
ential design is not required. A functional material can be semiconductor powder nanoparticles deposited arbitrarily on an irradiated surface. The specific working surface of the given facilities and the efficiency of their operation can be much greater than those of traditional planar photoelectric converters. The direct transformation of the energy of electromagnetic radiation into an electric current by means of bulk functional heterojunctions is an unresolved and topical problem that is now under active development. In particular, there are patents for photoelectric converters in the form of paint-and-lacquer coatings [1].

However, electromagnetic films are not the only alternative energy source. Methods for implementing electrochemical heterophase processes with electron transition through an interphase boundary are actively sought to produce electrical energy [2, 3]. As a rule, the channels whereby a solid body carries out the high-energy capture of a portion of energy in the events of adsorption, recombination, or other chemical transformations on its surface, which compete with single-quantum processes of vibrational-phonon, vibrational-electron, and vibrational-vibrational relaxations, are investigated.

Injection of “hot electrons”. In [4, 5], the mechanism by which electrical energy emitted during a heterogeneous, catalytic, and chemical reaction on its metallic surface is transferred to a semiconductor crystal is discussed. At a nanometer film thickness of less than 20 nm, “hot electrons” with energies of 1–3 eV reach the Schottky barrier ballistically, i.e., without energy loss, surmount it due to their kinetic energy, and enter the semiconductor, generating electric current in an external circuit. Thus, in this case, free charge carriers appear as a result of tunneling through the heterophase boundary from an external space. By analogy with photoelectromotive force [6], the energy transformation of heterogeneous exothermic chemical reactions received the name chemoelectromotive force (similar to the prefix photo-, chemoelectromotive force [7–9]). The prospects for its practical use are not yet clear because the chemical energy is inefficiently transformed into hot electron energy ($10^{-3}$–$10^{-5}$ electrons per chemical event) [7, 10]. Nevertheless, an analogous phenomenon has already found practical application in portable radioisotope power sources of radioelectric equipment [11–13]. Their principle of operation is based on the fact that a semiconductor crystal (acceptor) takes up electrons from radicals and ions generated in a liquid or gas working medium due to radiolysis [14, 15]. The maximum power of the given devices is several fractions of a microwatt, but the operating cycle duration exceeds 20 years at small sizes, justifying the means and making them indispensable for supplying active implants: cardioaccelerators, bioidentification microchips, RF identification devices of microsystems technology [16, 17], and so forth.

As in the case of hot electrons, the evident factor restricting the operation efficiency of radioisotope power sources is not only the small specific area of a functional heterojunction surface but also the small cross section of free charge-carrier capture by semiconductor crystals. The crystal’s electric field decays rapidly with interatomic distance from the surface. Hence, only a small fraction of particles ionized in the atmosphere can participate efficiently in the heterophase process on the “front” surface of a semiconductor crystal. From this viewpoint, it is of interest to employ dielectrics whose surfaces have high chemical activity. In the absence of a charge sink channel, the electrostatic field considerably exceeds the semiconductor field. The idea of this work is to apply nanoscale dielectric crystals with highly chemically active surfaces to chemical-electric conversion.

**EXPERIMENTAL**

Experiments were performed using nanopowders of the ZrO$_2$–Y$_2$O$_3$ (3 mol %) solid solution with an average particle size of about 7.5 nm (Fig. 1a). The powder was obtained via the coprecipitation of zirconium and yttrium chlorides with ammonia, followed by drying in a special-purpose microwave furnace ($T$ = 120°C and $t$ = 0.4 h) and sediment crystallization annealing at a temperature of 400°C for 2 h. The powder preparation technology was comprehensively reported in [18] and involves several stages. In accordance with Fig. 1b, the crystalline powder structure contains tetragonal and monoclinic phases (97 and 3%, respectively).

The samples were fabricated from the powder with the help of uniaxial compaction ($F_{\text{comp}} = 40$ MPa) in the shape of tablets (compacts), the diameter and height of which were, respectively, 20 and 3.2–3.3 mm (the weighed portion was $m = 1.2$ g). Afterward, the compacts were compressed by high hydrostatic pressure (500 Mpa) using the UVD-2 setup. Immediately before compaction, the powder was additionally dried in an exsiccator at $T = 120^\circ$C for 1 h to unification the initial physical conditions and, further, held in an environmental chamber at a humidity of $\eta = 70\%$ and temperature of $T = 21^\circ$C for 1 h. Upon the compact, the diameter and height of the compacts reduced on average to 16 and 2 mm, respectively. The tablet ends were mechanically covered with graphite electrodes. Immediately before the experiment, the samples were dried at 120°C for 1 h to synchronize the initial physical parameters, in particular, the moisture content.

The experiment was repeated threefold. The algorithm incorporated two steps. At the beginning, the time-dependent saturation of changes in the tablet mass $\Delta m = f(t)$, where $\Delta m = (m - m_0)/m$ and $m_0$ is the
dehydrated tablet mass, were recorded by means of an ADS50 moisture meter at the relative humidity $\eta = 75\%$, an atmospheric pressure of 760 mmHg, and room temperature $T_R = 19^\circ$C. Subsequently the samples were again dried under the same conditions and loaded with the resistive load $R_L = 1$ M$\Omega$. Afterward, the time dependences of the potential difference across the electrodes, $U = f(t)$, were recorded at 10-min intervals with the help of a JT-87 precision device operating in the microvoltmeter mode.

Clamping brass contacts were fastened on the sample before its placement inside the climatic chamber. To create a gradient in the flow of adsorbing molecules, one of the tablet ends was waterproofed by depositing a water-proof paraffin coating. The external view of the working cell with the sample is presented in Fig. 2.

The obtained experimental time dependences $U$ and $\Delta m$ were averaged and filtered. The data on $U = f(t)$ were filtered using the Ramer‒Douglas‒Peucker algorithm, also known as the iterative point-end fit algorithm [19, 20]. After verification and mathematical processing, the experimental dependences constructed by means of the Origin 6.0 program, were used to calculate the dependences $U = f(\Delta m)$ and the areas under the curves.

The spatial and structural organizations of the samples were investigated via scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with the help of JEM 200A and JSM640LV instruments, respectively, and according to the preparation technique described in [21]. The phase compositions of the powders were studied using a PANalytical Empyrean X-ray diffractometer, and the spectra were calculated and analyzed by means of PANalytical FullProf and HighScore Plus specialized crystallographic programs.

In defining how nitrogen molecules are thermally adsorbed or desorbed by porous objects (a Sorbi 4.1 device), the chemical activity of the sample surfaces was analyzed using the Brunauer–Emmett–Teller (BET) method.

**Fig. 1.** (a) TEM image of the $\text{ZrO}_2$–$\text{Y}_2\text{O}_3$ (3 mol %) nanopowder annealed at 400°C for 2 h and (b) its diffraction pattern.

**Fig. 2.** Sample under study: tablet 1 with carbon contacts 2 and paraffin coating 3.
RESULTS AND DISCUSSION

Figure 3 illustrates the time dependences of the emf and variations in the sample mass. As can be seen, the time dependence of variations in the mass is steady, and the process reaches saturation at approximately \( t = 100 \text{ min} \). Over the given period, the sample absorbs moisture from the atmosphere, which is equal to \( \approx 4\% \) of its mass in the dehydrated state. Over \( \approx 20 \text{ min} \) (the first stage), the interelectrode potential difference \( U(t) \) increases by \( \approx 110 \text{ mV} \). Unlike the dependence \( \Delta m(t) \), the dependence \( U(t) \) is nonmonotonic. Over a subsequent 80-min period (the second stage), a decrease in the interelectrode potential difference is observed, and the emf polarity inverts. The oppositely polarized signal amplitude is about 25\% of the total emf amplitude. In accordance with the emf-curve shape (Fig. 3), it can be concluded that the electrochemical process occurring in the sample has two stages.

Sample morphology. A typical SEM image of the sample fracture surface is depicted in Fig. 4. It can be seen that the microstructure is relatively porous. The calculated compact material density is \( \rho_c = 3.1 \text{ g/cm}^3 \), amounting to 40–50\% of the \( \text{ZrO}_2 \) ceramic density. It is clear that there is a branched network of relatively large (\( \approx 1 \mu\text{m} \)) pores. Thus, water easily percolates to the compact bulk. Most probably, gaseous water molecules first fill pores in the surface layer of the sample and then penetrate into its bulk with the delay being proportional to the flow resistance. Variations in the emf amplitude and its sign across electrodes are diagrammatically shown in Fig. 5.

In the initial state, the electrodes are separated by a dielectric interlayer made of dehydrated sample material and which have fixed potentials. An insignificant potential difference, which is induced during sample polarization upon compaction (the electret effect) is usually observed even in the initial state. In the case shown in Fig. 4, its value is about 20 mV. While sample wetting continues, the permeable electrode potential increases due to localization in the volume of the neighboring spatial region of free charge carriers by nonequilibrium chemical-electric processes [22]. However, the electrical resistance of the material layer between the electrodes is still large (according to impedance spectroscopy, its value is \( \approx 10^6–10^7 \Omega/\text{mm} \) (Fig. 5, stage I). The waterproof electrode potential remains fixed. When water molecules traveling along the sample capillaries begin to reach it, the sample conductance grows, shunting occurs, and the electrode potentials gradually equalize. The dependence (Fig. 3, curve 2) exhibits inflection and a gradual decrease in the potential difference. However, the water absorption dynamics remains virtually constant (Fig. 3, curve 1). The latter indicates that the generation of the system’s electrical energy is limited exclusively by the sample’s geometric features, rather than by the behavior of the mass exchange process.

Physical mechanism of the effect. In the case of a traditional functional heterojunction, emf generation assumes at least the formation of free charge carriers and their transport from the reaction volume to electrodes. Therefore, the mechanism whereby the emf appears on the electrodes of the sample under study must comprise not only the mechanism describing how charge carriers are created in the crystal lattice and localized near the nanoparticle surface but also the mechanism behind their transfer beyond the surface and the methods of delivery thereof to the sample electrodes.

Let us consider the possible mechanism by which free charge carriers are generated due to the absorption of neutral water molecules. On account of the electrical neutrality condition, it is supposed that the amounts of atmospheric negative and positive ions are identical and the atmosphere as a whole is electrically neutral.
In the substitutional solid solution based on zirconia, Y\textsuperscript{3+} impurity atoms have one electron less than Zr\textsuperscript{4+} atoms and are of the acceptor type, i.e., they create levels near the valence-band top in the band gap. Oxygen vacancies formed to compensate the excess volume and charges of the variable-valence impurity are electron donors, i.e., generate donor levels \( V \) near the valence-band bottom. For Y\textsuperscript{3+} and oxygen vacancies, the respective acceptor and donor characters of Zr\textsuperscript{4+} atoms and are of the acceptor type, i.e., they create electron donor levels near the valence-band top in the band gap. In other words, donors and acceptors coexist as bound charges, which are vacancy–impurity \((V^+–Y^{3+}^-)\) dipoles.

The donor and acceptor concentrations balance each other, and there is no deficiency (or excess) of electrons as compared to their amount needed to implement an ion bond. Hence, under normal conditions, the particle material is electrically neutral in the bulk and on the surface. An electric charge is in the bound state, and the bulk electron conduction is lacking.

In accordance with [26], adsorption adds the spectrum of adsorbate’s local levels (the impurity-type surface state) on the energy spectrum of nonadsorptive states [25]. According to the Shockley approximation [27], this signifies that a localized electron state with the energy \( E_a \) appears in the band gap if an electrically neutral molecule (e.g., H\textsubscript{2}O) is comes near. According to data from [28–30], the density of nonionized local states in a ZrO\textsubscript{2} film that is comparable in thickness with the diameter of the particle under study can be \( N_v \approx 5 \times 10^{24}–5 \times 10^{25} \text{ m}^{-3} \). In the band gap, the position of level \( E_a \) is determined predominantly by the characters of the lattice and sorbed molecule and the distances between the molecule and the surface [31]. When the distance, i.e., interaction length, increases, the corresponding level becomes more distant from the Fermi level. In the case of the acceptor level, an ejected electron of the atom of the nanoparticle’s crystal lattice is localized on it with the probability defined by Fermi–Dirac function (1), and adsorbate coupled by exchange interaction forces is fixed on the surface:

\[
f = \frac{1}{1 + \exp((E_f - E_a)/kT)}^{-1}.
\]

Theoretical calculations [32, 33] indicate that the maximum density of localized electron states corresponds to the depth \( E_f = 0.8 \text{ eV} \), i.e., is almost one order of magnitude less than the band-gap width of the crystal itself. Roughly speaking, a relatively weak bond between the impurity Y\textsuperscript{3+} and the vacancy \( V^+ \) is broken during the adsorption process.

However, free electron generation in the lattice and its localization near the surface are only a sufficient condition for an increase in the conductance of the near-surface layer of nanoparticles. To perform work in the external circuit, an electron must escape from the nanoparticle.

The mechanism behind electron transport from the nanoparticle can be explained if the generalized surface of the contact between solid (nanoparticle material) and gas phases is considered from the viewpoint of the theory of contact phenomena in semiconductors. The chemical interaction of water molecules with the generalized surface of nanoparticles is interpreted as an electric contact between particle materials with different electron work functions. In the case of an adsorbed molecule, the work function is equal to the potential of its ionization. For OH groups, this quantity is \( A_{\text{OH}} = I_{\text{OH}} = 13 \text{ eV} \) [34]. In the case of zirconia, the work function can be \( A_{\text{ZrO}_2} = 3–5 \text{ eV} \) [35, 36]. When the difference between work functions is \( \Delta A \approx 8–10 \text{ eV} \), the difference in the potentials between interacting unit charges on both sides of the heterophase boundary, i.e., \( \Delta \varphi_c = \Delta A/e \), where \( e \) is the elementary charge, is \( \Delta \varphi_c \approx 8–10 \text{ V} \).

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**Fig. 5.** Diagram characterizing the dependence of the emf sign (a) on the depth of moisture penetration into the sample (b). Here, \( \varphi_1 \) and \( \varphi_2 \) are the potentials of the moisture-proof and hydroscopic electrodes, respectively. Vector \( \mathbf{h} \) indicates the direction of water-molecule propagation through the sample bulk.
strength between them is calculated as \( E = \Delta \varphi/(h) \), where \( h \) is the averaged bond length of the adsorbate with a generalized surface. In the case of chemical adsorptive interaction, the bond length is comparable with the interplanar spacings of the crystal lattice in the solid body. For the tetragonal modification of the crystal lattice of zirconia, these lengths are \( h = 0.33-0.51 \text{ nm} \) ((111) and (110) planes, respectively). The electric-field strength between contacting materials will be no less than \( E_{\text{min}} \approx 1.6 \times 10^{10} \text{ V/m} \). This field is large enough to displace the electron density toward adsorption layer and partially evacuate electrons to the ion atmosphere, e.g., with the help of the thermal field emission mechanism.

As a result of contact with an adsorptive atmosphere, the nanoparticle surface recharge leads to the the nanoparticle’s dielectric volume polarization. Therefore, the maximum number of electrons that can be removed beyond the limits of the nanoparticle is determined by the permeability of its material. Hence, when \( \text{ZrO}_2 \) nanoparticles were used as the material characterized by a combination of the high dielectric permeability for oxides (\( \varepsilon = 25 \)) and a high chemical activity, this served the purpose thereof and we succeeded in experimentally recording the chemocurrent and the potential difference under the condition that the bulk structure adsorbs moisture.

**Thermodynamics of the process.** From the viewpoint of band theory, electrons move to impurity levels under the action of the thermal energy of the external thermostat. Adsorption occurs due to the uncompensated orbitals of valence electrons, i.e., because of an excess in the free surface energy. During adsorption process, the surface energy decreases and, on the contrary, the free energy (potential electrical energy) of the material volume increases at the expense of polarization. Thus, the system by adsorption converts the energy of an external thermostat and free surface energy into electric current. In fact, thermal and chemical energies are transformed into electric one.

In contrast to photocatalytic systems, nanopowder heterophase systems are thermodynamically closed, i.e., have a certain physical limit of electron production. Process saturation occurs if uncompensated valence bonds are saturated. Hence, such chemical-electric converters can operate only in the dynamic mode, i.e., under the condition of cycling of atmospheric moisture. The amount of energy that can be converted by the system during one cycle is proportional to the electric-field strength between the surface and the material bulk, i.e., is restricted by material dielectric permeability \( \varepsilon_{\text{ZrO}_2} \).

The system efficiency can be estimated under the assumption that the specific interface between solid and gas phases remains constant during adsorption. When measured via the BET method at a relative air humidity of \( \eta = 35\% \), the specific surface of the powder sample with a mass of 0.2236 g was 113.8 ± 6.8 m²/g. The mounting area of an OH group is \( S_{\text{OH}} = 10.2 \AA^2 = 10.2 \times 10^{-20} \text{ m}^2 \) [37, 38]. After completion of saturation, the sample’s water mass is \( m_{\text{water}} = 0.049 \text{ g} \). The molar mass of the OH group is \( M_{\text{OH}} = 17 \text{ amu} \). In the sample, the amount of water moles is \( N_{\text{H}_2\text{O}} = m_{\text{water}}/M_{\text{OH}} = 0.049/17 = 0.0028 \text{ mol} \), and the number of OH molecules is \( N_{\text{H}_2\text{O}} = N_A N_{\text{H}_2\text{O}} = 6.02 \times 10^{23} \times 0.0028 = 1.69 \times 10^{21} \), where \( N_A \) is the Avogadro number. When each adsorption interaction event leads to the generation of an electron, the maximum energy that can be released by the system during one cycle is \( W = N_{\text{H}_2\text{O}} e \Delta \varphi \). At \( \Delta \varphi = 50 \text{ mV} \), \( W = 1.69 \times 10^{21} \times 1.6 \times 10^{-19} \times 5 \times 10^{-2} \text{ C} \times 13.5 \text{ J} \). The real work performed by the system can be found using the area under the curve (Fig. 3): \( W' = \int U(t) dt/R \). At \( U(t) = (2026 + 1717) \times 10^3 \text{ V} \times 60 \text{ s} = 3743 \times 10^{-3} \text{ V} \times 60 \text{ s} = 49284 \text{ B}^2/7200 \times 10^6 \text{ V} = 6.85 \times 10^{-4} \text{ J} \). A comparison between the quantities \( W \) and \( W' \) indicates that only \( 5 \times 10^{-5} \% \) of adsorbing atoms participate in energy conversion. Probably, the system efficiency can be substantially increased by optimizing the geometry and structure of a functional medium.

**CONCLUSIONS**

The new electrokinetic size effect consisting in the production of an electrical energy (\( \Delta U = 130 \text{ mV} \) on a load of 1 M\( \Omega \)) by a compact sample of nanoparticles of the \( \text{ZrO}_2–\text{Y}_2\text{O}_3 \) (3 mol %) solid solution upon atmospheric moisture adsorption—is revealed.

A physical model explaining the mechanism of the above effect, which relies on the concepts of band theory and the theory of contact phenomena in semiconductors, is proposed. On the basis of the given model, it is inferred that an electrically neutral system can produce electric current carriers due to heterophase interactions accompanied by energy conversion from one type to another. In particular, it is demonstrated that, in the adsorption process, the thermal energy of an external thermostat and the free surface energy of nanoparticles are transformed into electrical energy. The driving force of the process is the difference between the work required to release an electron from the material of nanoparticles and the ionization energy of gas phase molecules.

From the results of the given work and published data, an inference is made that a high specific area and thermodynamic nonuniformity of an oxide nanopowder-system surface play an appreciable role in the efficient conversion of thermal and chemical energies into electrical energy.

The presented experiment can provide grounds for developing new types of energy converters, in particular, devices whereby the energy of the chemical interaction between atmospheric moisture and the...
nanoporous surface of solid bodies is converted into electric current. The given devices are of special interest because they allow unrestricted scaling into the low-size range and can have both bulk and planar designs. The latter makes them promising for the development of the circuitry of printed electronics and microsystems technology.

ACKNOWLEDGMENTS

This study was performed in the scope of the H2020/MSCA/RISE/HUNTER/691010 project and supported by the Russian Foundation for Basic Research, project no. 16-33-50010.

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Translated by S. Rodikov