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KINETICS OF RADIATION-HETEROGENEOUS AND CATALYTIC PROCESSES OF WATER IN THE PRESENCE OF ZIRCONIA NANOPARTICLES

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Abstract. The review of the results of research, development and use of nanomaterials in the nuclear-power engineering and technology have been presented. The basic properties of nanostructured materials are given. The prospects for the use of nanomaterials in the nuclear-power engineering, associated with the creation of nanostructured materials and coatings for structural elements of nuclear-power engineering plant and future thermal nuclear reactor to increase hardness and strength characteristics, raising corrosion and radiation resistance have been considered. The radiation- heterogeneous processes of water decomposition zirconium dioxide (n-ZrO_2) nanoparticles have been studied. The kinetics of buildup of molecular hydrogen in the radiolytic processes of water decomposition has been examined. The kinetics of molecular hydrogen accumulation at a gamma radiolysis of water on n-ZrO_2 surface is investigated. Influence of gamma radiations on n-ZrO_2+H_2O systems is studied at various temperatures T=373÷673K. Values of rates of molecular hydrogen accumulation at radiation, radiation-thermal and thermal processes are defined. Deposits of thermal and radiation-thermal processes at accumulation of molecular hydrogen in contact of n-ZrO_2 with water are revealed.

Keywords: *Nano zirconium oxide, radiolysis, energetic yield of water, kinetics, temperature, γ-radiation.*

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1. Introduction

Now the special attention to production of new technologies on production of dioxide of zirconium is paid. Dioxide of zirconium is used in metallurgy for receiving zirconium which is applied in nuclear reactors as constructional material. Development of a new electricity generation techniques is one of the most relevant tasks, especially nowadays under conditions of extreme growth in energy consumption. The exothermic heterogeneous electrochemical energy conversion to the electric energy through interaction of the ZrO_2 based nanopowder system with atmospheric moisture is one of the ways of electric energy obtaining. The questions of conversion into the electric form of the energy of water molecules adsorption in 3 mol% Y_2O_3 doped ZrO_2nanopowder systems were investigated using the density functional theory calculations. Based on the example of a nanopowder system ZrO_2–3% mol Y_2O_3 with atmospheric humidity interaction, the possibility of exothermic heterophase electrochemical energy conversion to electric energy is shown.

Electrical properties and structure of the experimental sample were studied under gradient molecular flux density of humidity during sample saturation. The idea of development of the novel chemo-electronic converter device based on nanoscale dielectrics as ZrO_2– 3% mol Y_2O_3 is proposed. The exothermic heterogeneous electrochemical energy conversion to the electric energy through interaction of the ZrO_2 based nanopowder system with atmospheric moisture have been 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% Y_2O_3 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 (Doroshkevich *et al.,* 2019; Subhoni *et al.,* 2018; Gridina *et al.,* 2019).

It possesses good strength, heat-insulating and dielectric properties in a wide interval of temperatures that in the turn allows to consider it as perspective material for production of the constructional materials (Cecal*et al.,* 2008; Garibov *et al.,* 2014; Garibov *et al.,* 2015; Guo & Chen, 2005; Whittle *et al.,* 2006; Bouvier *et al.,* 2000; LaVerne & Tandon, 2002; LaVerne, 2005; Caër *et al.,* 2005; Pikaev, 1975).

Use of dioxide of zirconium for fuel elements is caused by high ionic conductivity which is caused by transfer of anion oxygen vacancy. Nano dimensional systems in many respects differ from usual single-crystal systems therefore studying of their properties with water under influence of γ-radiations represents great practical and scientific interest (Muccillo *et al.,* 2017; Kojima *et al.*, 2006).

In this work for the purpose of identification of zirconium dioxide influence on water radiolysis, the kinetics of accumulation of molecular hydrogen at radiolytic decomposition of water in n-ZrO_2+H_2O system at various temperatures T = 373-673 K is investigated.

2. Experiment

Researches were conducted in static conditions in special quartz ampoules with volume V = 1 cm^3. As object of research it were used zirconium dioxide nanopowder samples purity of 99.9%, d = 20…30 nm, producing in "Sky Spring Nanomaterials, Inc.", USA.

Samples of dioxide of zirconium subjected to heat treatment at 573…673 K in the oxygen environment during 48 h. Then heat treatment was carried out alternately 1h in oxygen and 1h in vacuum (P ~ 10^{-2} Pa) during 12 h at 573…673 K. At the chosen processing modes in products of a radiolysis and a thermo radiolysis of water which can be formed in the presence of organic impurity, CO and CO_2 are absent. The amount of dioxide of zirconium in ampoules was made approximately by m = $3 \cdot 10^{-2}$ g.

For researches it was taken a distilledwater. Water into ampoules was entered by first method. In the first case in volume adsorptive device, water from a steam state adsorbed (H_2O_{abs}.) on a zirconium dioxide surface at T = 77 K. The amount of the entered water in ampoules corresponds to density of vapors of water in ampoules ρ = 5 mg/cm^3.

Accuracy of introduction of water to ampoules was made by 2%. Ampoules with samples by means of a cycle of cooling, pumping out and defrosting were deairated till a full cleaning of water from soluble oxygen and other organic compounds. Temperature when carrying out experiments was maintained with ±1 ^oC accuracy.

Radiation and radiation-thermal processes carried out on an isotope source of γ-quanta ^{60}Co. Power of the absorbed dose of gamma radiation is determined by ferrosulphate, cyclohexane and methane dosimeters (Pikaev, 1975; Garibov *et al.*, 2017; Agaev *et al.*, 2018).

The absorbed radiation dose in the studied systems is determined by the relation of their electronic density and dosimetric systems. Ampoules opened in special cell, from where products of a radiolysis came to a chromatograph column. The analysis of products of radiation and heterogeneous processes was carried out on the gas-chromatograph "Svet-102" and gas analyzer "Gazokhrom-3101".

3. Results and discussion

In the work the kinetics of the water radiolysis processes were investigated at various temperatures and gamma radiation on the nano-ZrO_2 surface. It has been established radiation-heterogeneous splitting processes of water with the combined effect of temperature and gamma rays on the surface of nano-ZrO_2 goes on electrophysical model with mechanism. Thus, on the basis of the received results it is possible to make the following conclusions. The kinetics of accumulation of molecular hydrogen at a gamma radiolysis of pure water and ZrO_2+H_2O system is investigated. Besides, the kinetics of accumulation of molecular hydrogen at radiation, radiation-thermal and thermal processes in contact of ZrO_2 with water is studied. Formation of the surface-active centers and secondary electrons from ZrO_2, causes increase inrates of saturation of molecular hydrogen at thermal and radiation-thermal processes in ZrO_2+H_2O system. Thus it is established that since $T \geq 373$ K there is also an accumulation of the thermal superficial active centers of water decomposition in ZrO_2 at thermal-radiation and thermal processes.

The kinetics of accumulation of molecular hydrogen at a heterogeneous radiolysis of water in the presence of zirconium dioxide is studied. It is revealed that at $T \geq 373$ K a dioxide of zirconium possesses thermocatalytic activity in the process of water decomposition (Pikaev, 1975). Hydrogen occurrence kinetics during water heterogeneous radiolysis with the participation of zirconium dioxide are given in Figure 1-4.

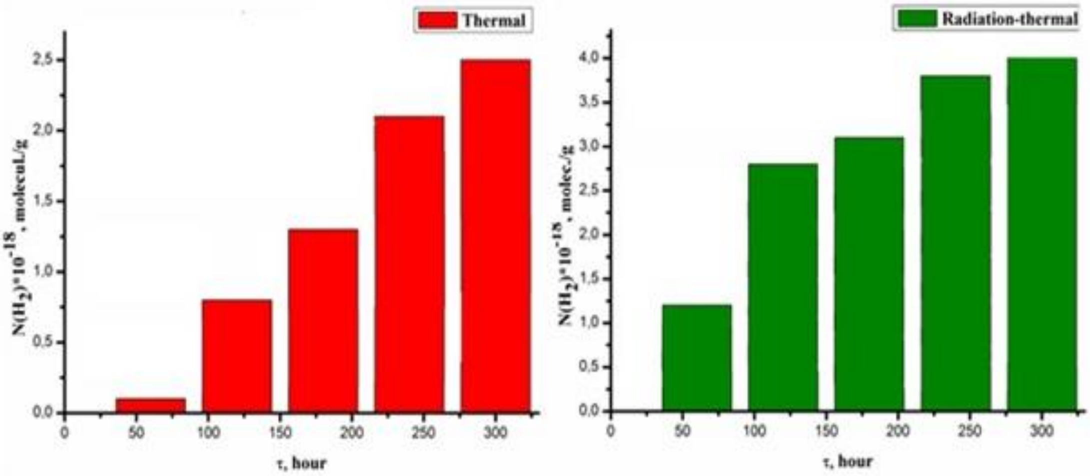

Fig. 1. Kinetics of accumulation of molecular hydrogen at thermal and radiation-thermal decomposition of water on a surface of n-ZrO_2 at the various temperature T = 373 K, ρ = 5 mg/cm^3, d_{ZrO2} = 20-30 nm, D = 0.32 Gy/s, $m_{ZrO2} = 3 \cdot 10^{-2}$g

In Figure 1 the speed of the process at T = 373 K temperature in the nano-ZrO_2+H_2O system is W_R= 7.8·10^{13} molecules/g·s, W_T= 1.38·10^{13} molecules/g·s, $W_{R/T}$= 9.17·10^{13} molecules/g·s, hydrogen energy yield $G(H_2)$ = 4.8 molecule/100 eV.

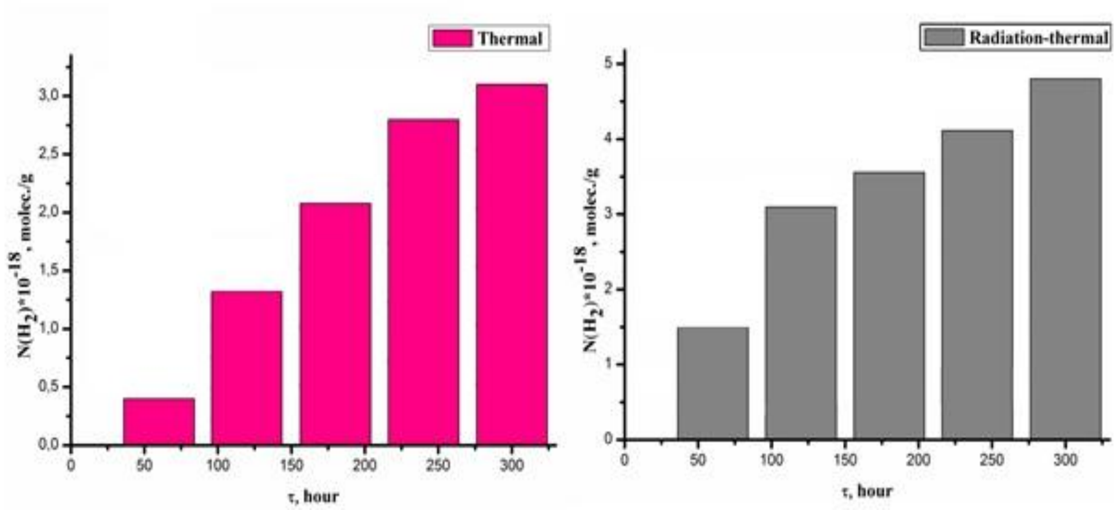

Fig. 2. Kinetics of accumulation of molecular hydrogen at thermal and radiation-thermal decomposition of water on a surface of n-ZrO_2 at the various temperature T = 473 K, ρ = 5 mg/cm^3, d_{ZrO2} = 20-30 nm, D = 0.32 Gy/s, m_{ZrO2} = 3·10^{-2} g

In Figure 2 the speed of the process at T=473K temperature in the nano-ZrO_2+H_2O system is W_R=1.52·10^{14} molecules /g·s, W_T=0.55·10^{14} molecules /g·s, $W_{R/T}$=2.08·10^{14} molecules /g·s, hydrogen energy yield $G(H_2)$=8.35 molecule /100eV.

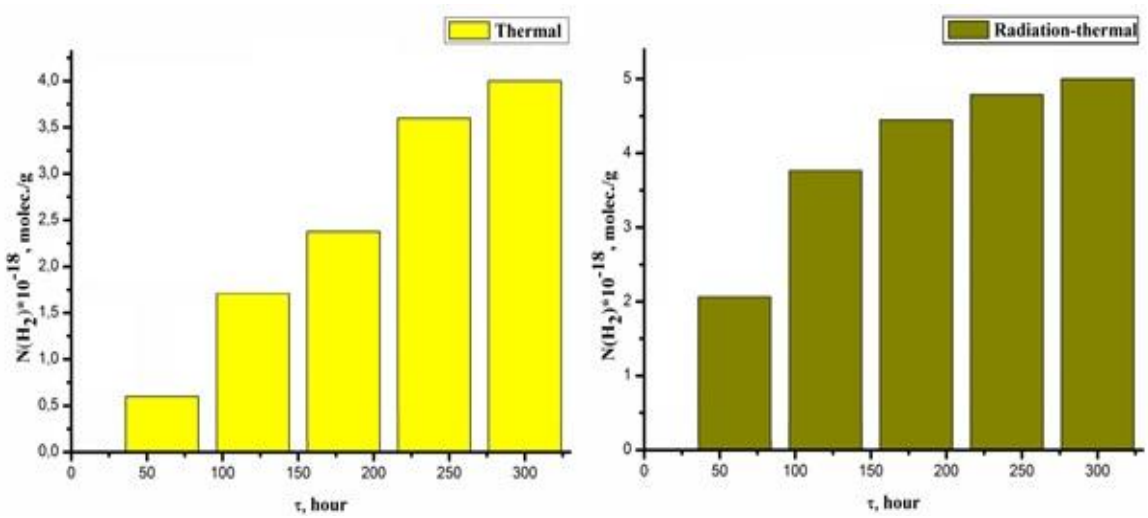

Fig. 3. Kinetics of accumulation of molecular hydrogen at thermal and radiation-thermal decomposition of water on a surface of n-ZrO_2 at the various temperature T = 573 K, ρ = 5 mg/cm^3, d_{ZrO2} = 20-30 nm, D = 0.32 Gy/s, m_{ZrO2} = 3·10^{-2} g

In Figure 3 the speed of the process at T=573K temperature in the nano-ZrO_2+H_2O system is W_R = 2.22·10^{14} molecules /g·s, W_T= 1.11·10^{14} molecules /g·s, $W_{R/T}$= 3.33·10^{14} molecules /g·s, hydrogen energy yield $G(H_2)$ = 13.6 molecule /100eV.

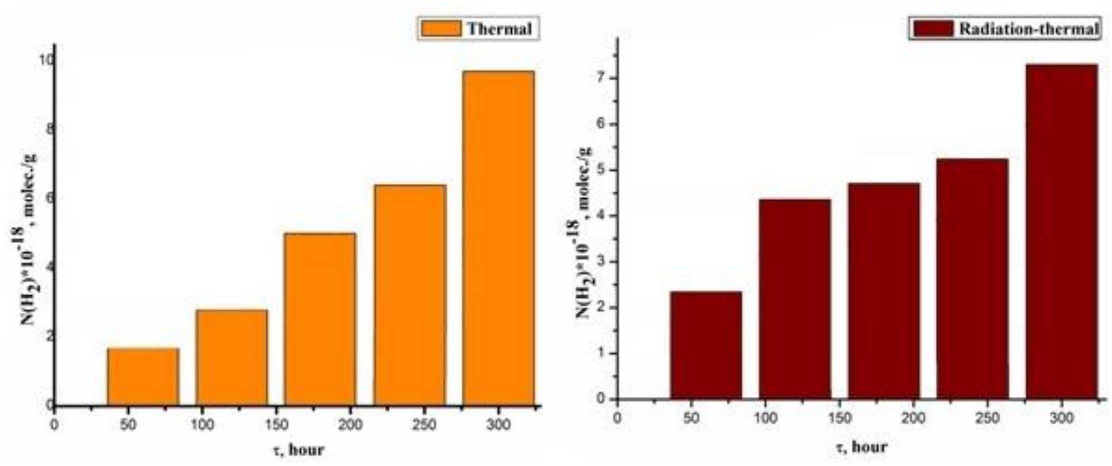

Fig. 4. Kinetics of accumulation of molecular hydrogen at thermal and radiation-thermal decomposition of water on a surface of n-ZrO_2 at the various temperature T = 673 K, ρ = 5 mg/cm^3, d_{ZrO2} = 20-30 nm, D = 0.32 Gy/s, $m_{ZrO2} = 3\cdot10^{-2}$ g

In Figure 4 the speed of the process at T=673K temperature in the nano-ZrO_2+H_2O system is W_R= $4.16\cdot10^{14}$ molecules /g·s, W_T = $2.78\cdot10^{14}$ molecules /g·s, $W_{R/T}$= $6.94\cdot10^{14}$ molecules /g·s, hydrogen energy yield $G(H_2)$ = 25.7 molecule /100eV.

Apparently, with increase in temperature the second slow stage of processes of accumulation of hydrogen which are observed at a radiation-heterogeneous radiolysis of water in the presence of zirconium dioxide at T = 373 K isn't observed. In all kinetic curves after certain time the stationary area is observed. The radiation component of radiation-thermal processes in a first approximation defined as a difference:

$$W_R(H_2) = W_{RT}(H_2)-W_T(H_2)$$

where $W_{RT}(H_2)$ – the rate of formation of molecular hydrogen at radiation-thermal process of decomposition of water, $W_T(H_2)$ - the rate of formation of molecular hydrogen at thermal process of decomposition of water, $W_R(H_2)$ - the rate of formation of molecular hydrogen at radiation processes. Values of radiation-chemical yields are determined by value of rates of the radiation component of radiation-thermal processes of water decomposition. The received values of rates and radiation-chemical yields of molecular hydrogen are given in Table1.

Table 1. Values of rates and radiation-chemical yields of molecular hydrogen at radiation-thermal, thermal and radiation processes of water decomposition in ZrO_2+H_2Oabs. system at various temperatures

Irradiated systems	Nano-ZrO_2, *d*, nm	*T*, K	$W_R(H_2)\cdot10^{14}$, molecule/g·s	$G(H_2)$, molecule/100eV
n- ZrO_2+$H_2O_{abs.}$	20-30	373	0.78	4.8
n- ZrO_2+$H_2O_{abs.}$	20-30	473	1.52	8.35
n- ZrO_2+$H_2O_{abs.}$	20-30	573	2.22	13.6
n- ZrO_2+$H_2O_{abs.}$	20-30	673	4.16	25.7

Comparisons of yield values of molecular hydrogen at radiation-heterogeneous processes in ZrO_2+$H_2O_{abs.}$system in the range of temperatures T = 373-673 K, shows that, temperature stimulates process of a heterogeneous radiolysis and the hydrogen yield linearly grows with temperature from 4.8 to 25.7 mol./100 eV.

On the basis of temperature dependence of rates of processes in the Arrhenius coordinates are defined a value of their activation energy. Dependences of rates of radiation-thermal and thermal processes of molecular hydrogen accumulation at radiation- heterogeneous processes of water decomposition in the presence of zirconium dioxide are given in Fig. 5-6.

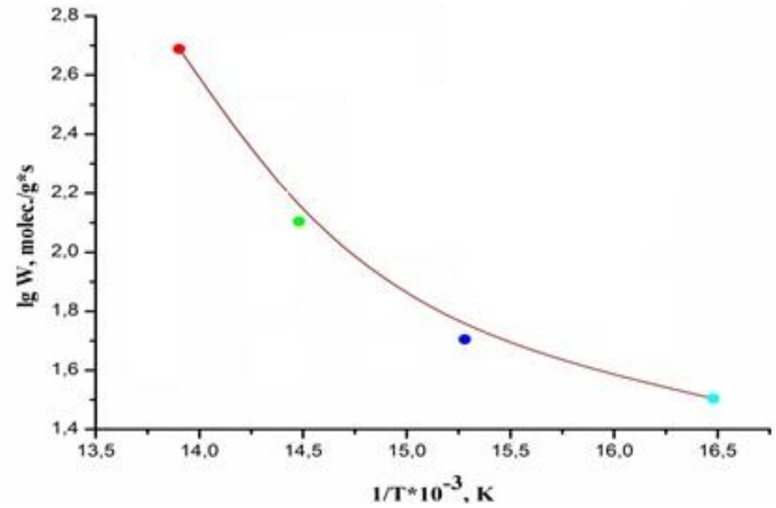

Fig. 5. Dependence of *lgW* on the reverse temperature at thermal decomposition of water in the presence of the nano-ZrO_2

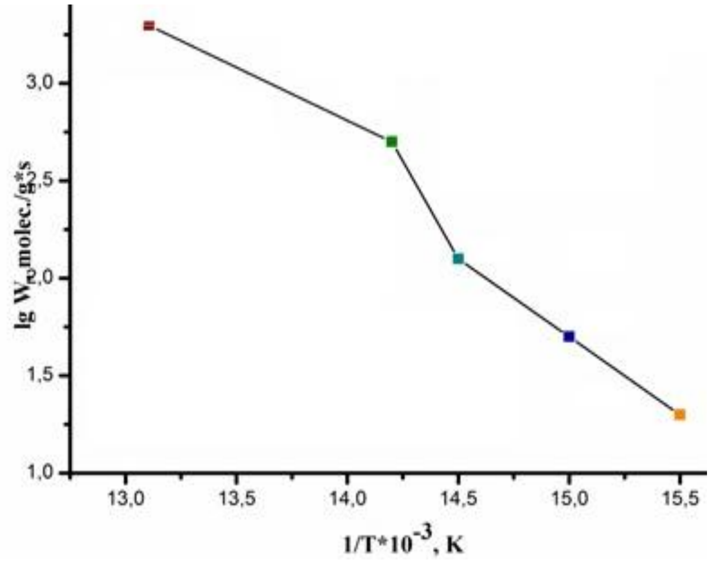

Fig. 6. Dependence of lgW on the reverse temperature at radiation – thermal decomposition of water in the presence of the nano-ZrO_2

Energy of activation of radiation-thermal and thermal processes of accumulation of molecular hydrogen are equal *Ea* = 25.2 and 38.5 kJ/mol respectively.

Apparently, energy of activation of thermal process of water decomposition in the presence of ZrO_2 is more, than radiation-thermal processes. At radiation-thermal processes of water decomposition the radiation generated active centers of a surface and secondary electronic radiations participate which possess bigger energy, than thermally active centers. Therefore, energy of activation of process of molecular hydrogen accumulation grows on a number of radiation-thermal and thermal processes.

4. Conclusion

Thus, on the basis of the received results it is possible to make the following conclusions. The kinetics of accumulation of molecular hydrogen at a gamma radiolysis of pure water and ZrO_2+H_2O system is investigated. It is established that the radiation-chemical yield for ZrO_2+H_2O system is more (G(H2)=2.14 mol./100 eV), than at radiolysis of a pure water (G(H2)=0.45 mol./100 eV). Besides, the kinetics of accumulation of molecular hydrogen at radiation, radiation-thermal and thermal processes in contact of ZrO_2 with water is studied. Formation of the surface-active centers and secondary electrons from ZrO_2, causes increase in rates of saturation of molecular Molecules/q·s hydrogen at thermal and radiation-thermal processes in ZrO_2+H_2O system. Thus it is established that since T $\geq$ 473 K there is also an accumulation of the thermal superficial active centers of water decomposition in ZrO_2 at thermal-radiation and thermal processes.

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