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Review

ELECTRICAL PROPERTIES OF HYDRATED VANADIUM COMPOUNDS

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Vanadium pentoxide gels have a layered structure, where V–O ribbons are separated by water that permit to intercalate a wide range of various ionic and molecular species into these gels. They have both ionic and electronic conduction. The ionic part is defined by proton diffusion and the electronic one by the electron hopping between vanadium ions of different valence states.

In this review the results of a complex study concerning the physical properties of a wide range of vanadium based hydrated compounds such as $H_2V_{12-x}Me_xO_{31\pm\delta}\cdot nH_2O$ (Me = Mo, Ti, Cr), $Me_2V_{12}O_{31\pm\delta}\cdot nH_2O$ (Me = Li, Na, K, Rb, Cs), and $MeV_{12}O_{31\pm\delta}\cdot nH_2O$ (Me = Mg, Ca, Ba) are presented.

The basic attention is given to the description of structure, synthesis, electrical properties, and valence conditions of metal ions in the xerogels.

Keywords: vanadium oxides, hydrates, physical properties

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1. Introduction

Transition metal oxides have been intensively studied because of their possible practical applications. Among them the vanadium oxides are important because the atom of vanadium has a non-occupied $3d$ electronic shell that causes the existance of various vanadium oxides and vanadium–oxygen based compounds. These materials can be separated into four groups: vanadium oxides, substitution and inculcation phases, glasses, and hydrates. The first three groups are studied rather well [1–3]. During the last twenty years the physical chemistry of vanadium hydrates has been developing intensively. From the physical point of view one of the most interesting features of these compounds is their unusually high conductivity in comparison with crystalline, amorphous V_2O_5, and glasses on its basis. The results of studies of properties of vanadium hydrates such as structure and chemical composition are summarized in [4–6].

In this paper the review of the last years study of these compounds performed in the Semiconductor Physics Institute (Vilnius, Lithuania) is presented.

2. Synthesis and structure

For the first time the preparation method of the hydrated V_2O_5 was described by Düllberg [7]. This method was based on the reaction between Na_3VO_4 and strong mineral acids. As a result of this reaction the red-brown sediment was produced and identified by Düllberg as the hydrated vanadium pentoxide $V_2O_5\cdot nH_2O$. Similar method is described in [8] where the vanadium hydrates were produced by interaction between HCl or H_2SO_4 and the solution of $NaVO_3$ or KVO_3. However, using these methods one cannot be sure that the produced hydrates do not contain metals Na or K. This problem was solved by Müller [9]. He suggested two methods. The first of them is the interaction of V_2O_5 and hydrogen peroxide and the second one is the fast quenching of the molten V_2O_5 into distilled water. Usually these two methods are used until now.

The fibres can be presented as flat tapes of 1000 Å length and 100 Å width [13] (see Fig. 2). As an example we will describe the first preparation method in accordance with [10]. This method is based on the sol–gel technological process [5]. The vanadium pentoxide powder is dissolved in the hydrogen peroxide at 273 K

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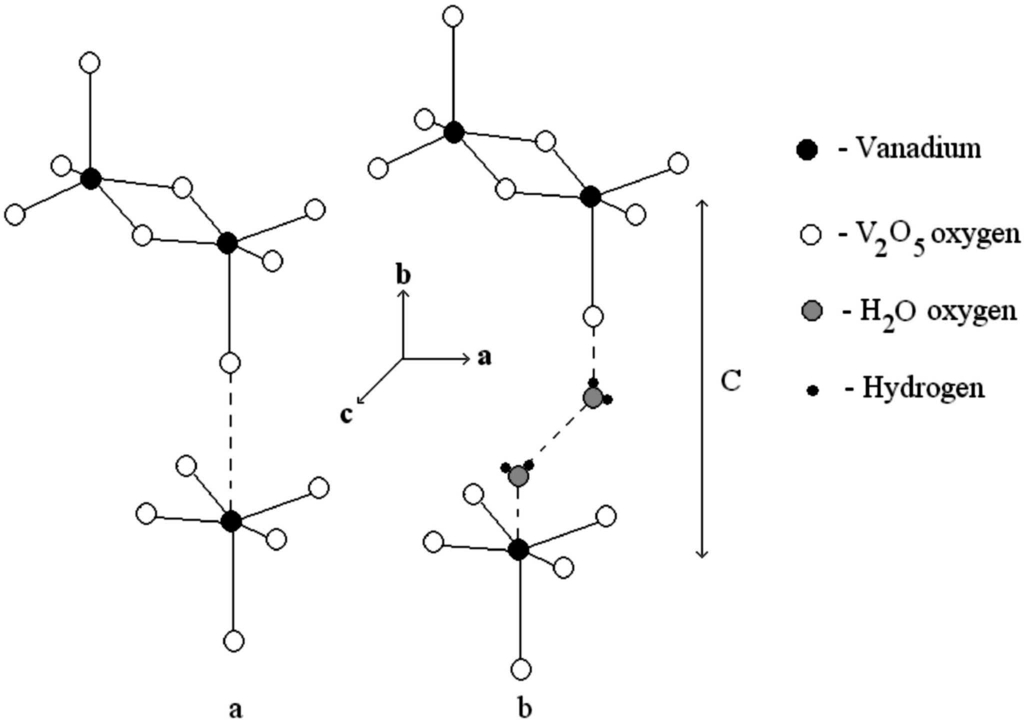


Fig. 1. Structure of (a) orthorhombic vanadium pentoxide [12] and (b) its xerogel [3].

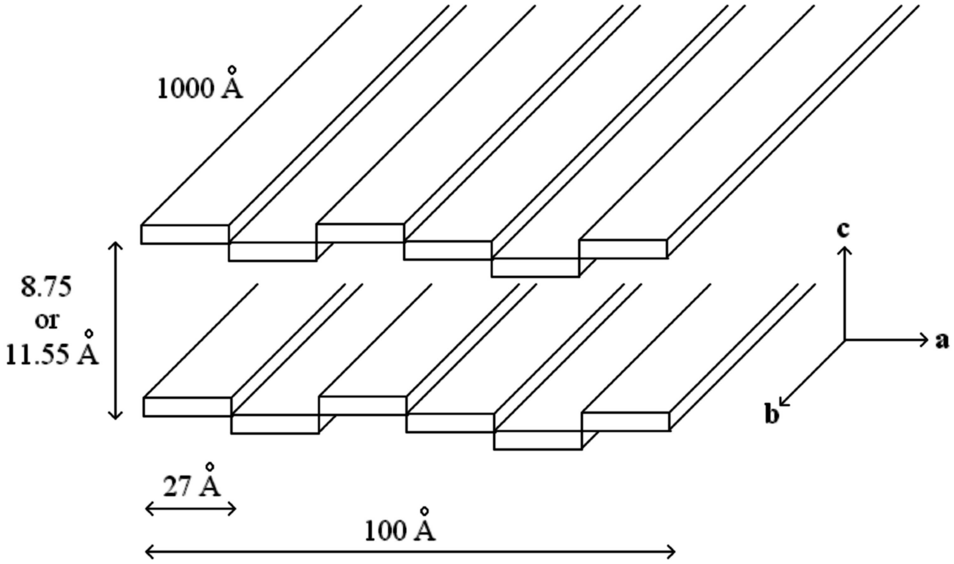


Fig. 2. Structural layers of vanadium pentoxide xerogels [13].

because this reaction is exothermic. Then the solution is heated at 353 K for 2 h for the dissociation of the vanadium peroxide complexes. Obtained gels are deposited on the substrate and baked at room temperature in air. Similar sol–gel technology is used for the preparation of the vanadium hydrates containing various metals and doping elements (see, for example, [10]).

X-ray study of the structure of hydrated V_2O_5 was first described in [11]. The structure has a layered character where V_2O_5 layers are formed by cross-linked fibres separated by water molecules. The structure of these fibres could be related to the V–O chains observed in bulk orthorhombic vanadium pentoxide [12] (see Fig. 1). The interlayer distance c depends on the water content in the hydrate. X-ray diffraction, DTA (differential thermal analysis), and GTA (gravimetrical thermal analysis) investigations of gels show that at room temperature the interlayer distance $c = 11.55$ Å that corresponds to the first phase $V_2O_5 \cdot 1.6\, H_2O$ of the hydrate. This phase slowly disappears with temperature and at ~393 K the second $V_2O_5{\cdot}0.5\,H_2O$ phase is observed. It presumably corresponds to the removal of weakly bonded water. The interlayer distance c = 8.75 Å in this case. Up to ~573 K the chemically bonded water is removed from the xerogel and the crystallization of the vanadium pentoxide takes place. So, the dehydration process of the gels may be written as

$$V_2O_5 \cdot 1.6\,H_2O \overset{393\text{ K}}{\longrightarrow} V_2O_5 \cdot 0.5\,H_2O \overset{573\text{ K}}{\longrightarrow} V_2O_5\,. \quad (1)$$

A more detailed study of the dehydration by means of IR spectroscopy method shows that the hydrated vanadium gels by nature are polyvanadic acids the chemical formula of which can be written as $H_2V_{12}O_{31}{\cdot}nH_2O$ or $(H_3O)2V_{12}O_{31}{\cdot}nH_2O$ [10]. All three formulas $V_2O_5{\cdot}nH_2O$, $H_2V_{12}O_{31}{\cdot}nH_2O$, and $(H_3O)2V_{12}O_{31}{\cdot}nH_2O$ are used in the literature.

3. Physical properties

3.1. Electrical conductivity

3.1.1. General

One of the features of hydrated vanadium compounds is their unusually high conductivity in comparison with crystalline, amorphous V_2O_5 and glasses on its basis. For the first time the semiconducting properties of vanadium pentoxide gels were described in [14]. Now it is established that the conductivity of hydrates consists of two components – electronic and ionic. The electronic part is determined by electron jumps between various valence vanadium ions and the ionic one is due to proton diffusion [15, 16]. Synthesis and studying of physical properties of various compounds on the basis of vanadium pentoxide gels, performed in the last years, allows describing and understanding in more detail the kinetic phenomena in this class of substances.

Hydrated vanadium compounds are the typical materials obtained by "soft" chemistry methods [5] that allow to prepare the films of various thicknesses in a simple way; V–O layers thus are oriented in parallel to the substrate. Electrical conductivity measurements in parallel ($\sigma_=$) and perpendicular ($\sigma_\|$) directions to layers have shown the presence of significant anisotropy. At room temperature $\sigma_\| = 1.3{\cdot}10^{-3}$ S/m and $\sigma_= = 44$ S/m, when the reduced vanadium ions content given by the ratio $C = V^{4+}/(V^{4+} + V^{5+})$ (V^{4+} and V^{5+} are the concentrations of V^{4+} and V^{5+} ions respectively) is equal to 0.097 [15]. Electrical conductivity of gels increase with C, that illustrates Fig. 3 [15]. The general features for the conductivity dependence on $1/T$ for all C values are similar: there are low and high temperature ranges (LT and HT respectively), where $\ln(\sigma T)$ varies linearly with $1/T$, and an intermediate temperature range, where the slope of $\ln(\sigma T) = f(1/T)$ curve changes continuously. Using the small radius polaron conductivity theory, the activation energy of the conductivity for HT range may be written as

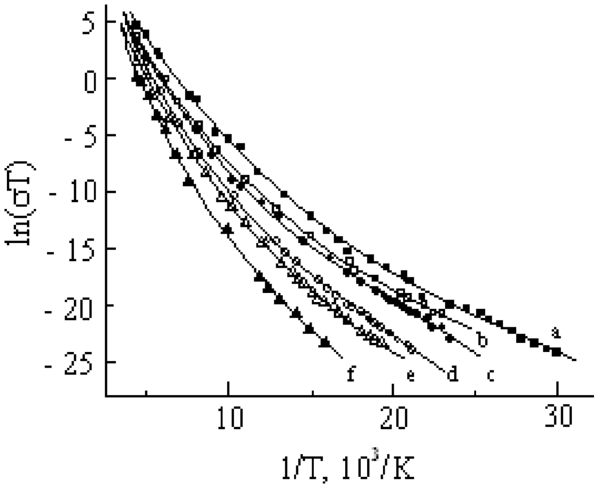


Fig. 3. Electrical conductivity versus temperature for vanadium xerogels containing various reduced vanadium ions content C: *a* at 0.097, *b* at 0.059, *c* at 0.039, *d* at 0.023, *e* at 0.013. Curve *f* was obtained with a polymerized gel (C = 0.005) [15].

$$E_{\mathrm{HT}} = \frac{W_{\mathrm{P}} - W_{\mathrm{D}}}{2} - J\,, \quad (2)$$

where W_{P} is the energy of polaron creation, W_{D} is the so-called Anderson's disorder energy, and J is the transfer integral [17]. From the results presented in Fig. 3, E_{HT} = 0.35–0.18 eV that practically is equal to the results for amorphous and crystalline V_2O_5 [18–20]. For the LT range E_{LT} = 0.043–0.103 eV. In this case the activation energy may be written as

$$E_{\mathrm{LT}} = \frac{W_{\mathrm{D}}}{2} - J\,. \quad (3)$$

A detailed theoretical treatment has been given by Schnakenberg [21] and the conductivity versus temperature may be written as

$$\sigma T = D\,\nu_0 \exp\left[-\frac{2W_{\mathrm{P}}}{h\nu_0}\tanh\frac{h\nu_0}{4kT}\right] \times \exp\left[-\frac{W_{\mathrm{D}}/2 - J}{kT}\right], \quad (4)$$

where D is a constant characteristic of the material and polaron hopping and ν_0 is a mean optical phonon frequency. In the Table 1 the values of E_{HT}, E_{LT}, W_{P}, $h\nu_0$, and γ (the constant of the electron–phonon cou-

Table 1. Values of E_{HT}, E_{LT}, W_{P}, $h\nu_0$, and γ for various reduction ratios C of the vanadium ions [14].

C	E_{HT}, eV	E_{LT}, eV	W_{P}, eV	$h\nu_0$, eV	γ
0.005	0.35	0.103	0.49	0.052	9.7
0.013	0.25	0.069	0.37	0.035	10.4
0.029	0.26	0.076	0.37	0.040	9.8
0.039	0.23	0.065	0.33	0.037	8.9
0.059	0.22	0.050	0.34	0.034	10.0
0.097	0.18	0.043	0.28	0.026	10.8

pling) for various reduction ratios C of vanadium ions are presented [14].

3.1.2. Concentration and mobility of the carriers

The first data on the carrier concentration in the vanadium pentoxide xerogels have been obtained from the low frequency current fluctuations measurements in the frequency range from 20 Hz to 10 kHz [22]. The concentration of the carriers was calculated from the empirical formula for the noise such as f^{-1}, for which the spectral density of the noise

$$S(f) \sim \alpha f^{-1}\,, \tag{5}$$

where $\alpha = 2{\cdot}10^3$ is the so-called Hooge constant [23]. The calculated values of the concentration are in the range 10^{23}–$6{\cdot}10^{24}$ m^{-3}. However, it is shown that for the hopping conductivity, which takes place in the xerogels, the values of the Hooge constant are close to 1 [24], that allows to speak about a higher concentration of the carriers.

The first data on the concentration and mobility of carriers of a current for vanadium hydrated compounds are presented in [25–27] where from three independent experiments – the measurements of the frequency dependences of the conductivity (G) and capacity (C) of the polyvanadium–molybdenum acid thin films, the investigations of the Cole–Cole diagrams, and the measurements of the time dependences of the transitive currents $I(t)$ – the mobility of carriers along ($\mu_{=}$) and across ($\mu_{\|}$) the V–O layers have been determined. The results are summarized in Table 2. The concentrations of carriers are identical for all samples and equal to $(1.2 \pm 0.8){\cdot}10^{25}$ m^{-3}. In Fig. 4 the temperature dependences of mobility $\mu_{\|}$ and concentration n for the $H_2V_{10}Cr_2O_{31.7}{\cdot}8.6\,H_2O$ xerogel are shown [26], whence it follows that the concentration practically does not depend on the temperature. In Fig. 5 the temperature dependences of the conductivities across ($\sigma_{\|}T$) and along ($\sigma_{=}T$) the V–O layers are presented [26]. The conductivity activation energies are $\Delta E_{\|}$ = (0.205 ± 0.006) eV and $\Delta E_{=}$ = (0.209 ± 0.010) eV. The mobility activation energy, determined from Fig. 4, is $\Delta E_{\mu T}$ = (0.217 ± 0.008) eV. Within the limits of errors the activation energies of the conductivity and mobility are the same. Hence the temperature dependence of conductivity basically is defined by the temperature dependence of mobility.

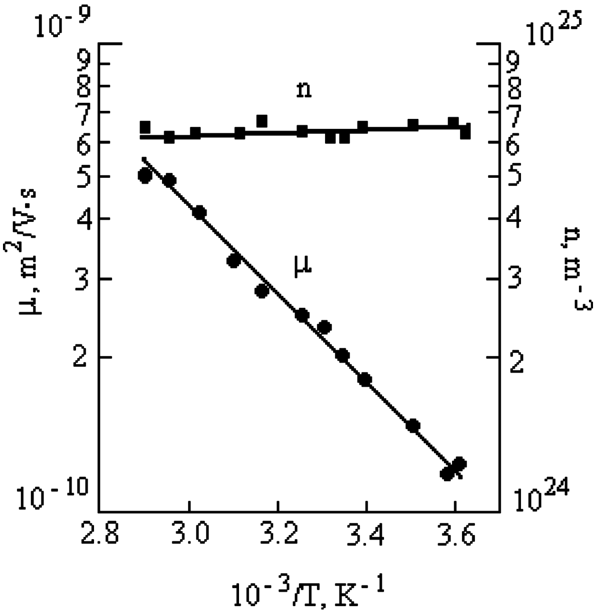


Fig. 4. Carrier mobility and concentration along V–O layers versus temperature for $H_2V_{10}Cr_2O_{31.7}{\cdot}8.6\,H_2O$ xerogel [26].

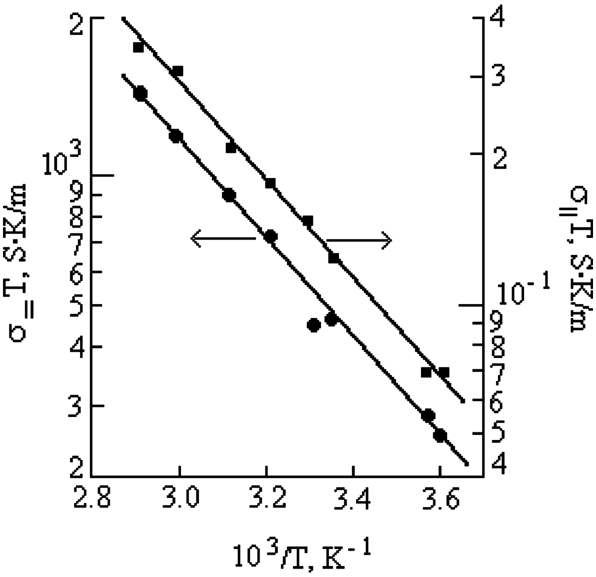


Fig. 5. Temperature dependences of the conductivity across ($\sigma_{\|}T$) and along ($\sigma_{=}T$) the V–O layers for $H_2V_{10}Cr_2O_{31.7}{\cdot}8.6\,H_2O$ xerogel [26].

Table 2. Carrier mobility in polyvanadium–molybdenum acid xerogels along ($\mu_=$) and across ($\mu_\|$) the V–O layers [25–27].

Method of the measurements	Mobility, $m^2/(V\,s)$	
	$H_2V_{11.5}Mo_{0.5}O_{30.7}\cdot 8.4\,H_2O$	$H_2V_{10}Mo_2O_{31.7}\cdot 8.6\,H_2O$
$G(f)$ and $C(f)$ measurements		$\mu_\| = 2\cdot 10^{-12}$
Cole–Cole diagrams	$\mu_\| = 1.4\cdot 10^{-12}$	$\mu_\| = 0.9\cdot 10^{-12}$
$I(t)$ measurements	$\mu_\| = 1.4\cdot 10^{-12}$, $\mu_= = 0.9\cdot 10^{-8}$	

3.1.3. Anisotropy of the conductivity

From Fig. 5, the anisotropy coefficient, defined as

$$K = \frac{\sigma_=}{\sigma_\|}\,, \tag{6}$$

is equal to $\sim 3.5\cdot 10^3$. As mentioned in 3.1.1, the electronic part of conductivity is defined by the electron jumps between the various valence vanadium ions [15, 16]. In the polar materials, such as the transitional metals oxides, with the strong electron–phonon coupling, the small radius polarons are formed at temperatures $T > \Theta/2$, where Θ is the Debye temperature. For the nonadiabatic case, the probability P for the electrons to jump over the distance R may be written as

$$P = \nu \exp\left[-2\alpha R - \frac{W_P - W_D}{2kT}\right], \tag{7}$$

where ν is the frequency of the jumps and α is the decay of the wave function. On the other hand, the hydrated compounds are two-phase systems (electronic and protonic), for which the total resistivity ρ may be written as [28, 29]

$$\rho = \rho_A^{1-\xi}\,\rho_B^{\xi}\,, \tag{8}$$

where ρ_A and ρ_B are the resistivities of the A and B phases respectively (in our case these are the resistivities of the electronic and protonic parts of the conductivity). From (7) and (8), as it has been shown in [30], the conductivity σ_i of both the single vanadium pentoxide crystals and hydrates in the i direction (the crystallographic directions a, b, and c for the single crystals or the direction along and across the V–O layers for the hydrates) may be written as

$$\sigma_i = \langle\sigma\rangle R_i^2\,\frac{\exp[-2\alpha(R_i - \langle R\rangle)]}{\langle R_2\rangle}\,, \tag{9}$$

where R_i is the hopping distance in the i direction, $\langle\sigma\rangle = (\sigma_a\sigma_b\sigma_c)^{1/3}$ for the crystals and $\langle\sigma\rangle = (\sigma_=\sigma_=\sigma_\|)^{1/3}$ for the hydrates ($\sigma_=$ and $\sigma_\|$ are conductivities along and across the V–O layers accordingly), $\langle R\rangle = (a + b + c/2)$, and $\langle R_2\rangle = (abc/2)^{2/3}$. Figure 6 presents the dependence of the logarithm of reduced conductivity $Y_i = \ln(\langle R_2\rangle\sigma_i/\langle\sigma\rangle R_i^2)$ on the distance between vanadium ions $X_i = R_i - \langle R\rangle$ in the i direction [30]. It is clear that as for the single crystals and xerogels the mentioned dependence is exponential in accordance with (9), the anisotropy of the conductivity in both cases can be explained by the anisotropy of the tunnelling term $\exp(-2\alpha R)$ in the expression (7) for the probability P of the electron jump over the distance R.

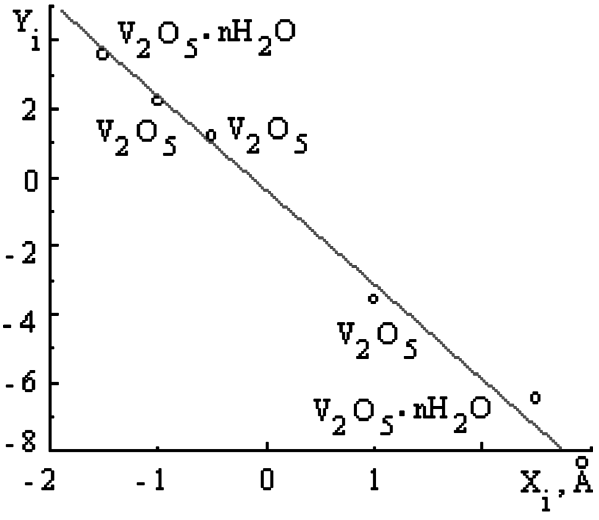


Fig. 6. Logarithm of reduced conductivity (Y_i) dependence on the distances between vanadium ions (X_i) for the xerogels $V_2O_5\cdot nH_2O$ and oxides V_2O_5 [30].

3.1.4. Conductivity and phase transitions

The conductivity dependence on the temperature, which Fig. 1 illustrates, corresponds to the temperature range 23–250 K. The results of the conductivity investigations at the highest temperatures are described in [31, 32]. It has been shown that for $M_2V_{12}O_{30.7}\cdot nH_2O$ (M = Li, K, Na) and $MV_{12}O_{30.7}\cdot nH_2O$ (M = Mg, Ca, Sr, Ba) xerogels at the temperature in the interval 332–351 K the conductivity activation energy changes from 0.26–0.31 eV to 0.57–0.68 eV (see Fig. 7). It can be explained by the partial dehydratation of the samples. More detailed investigation of this phase transition is presented in [33]. As mentioned in 3.1.3, the probability P for the electron to jump over the distance R may be written as formula (7). In the transition metal oxides the wave functions are strongly localized. In

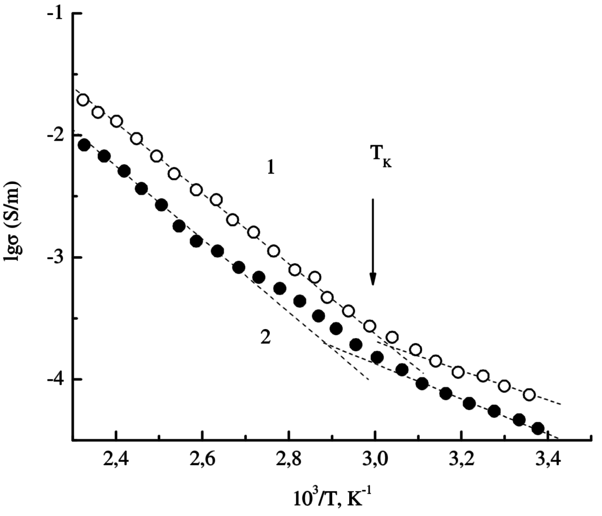
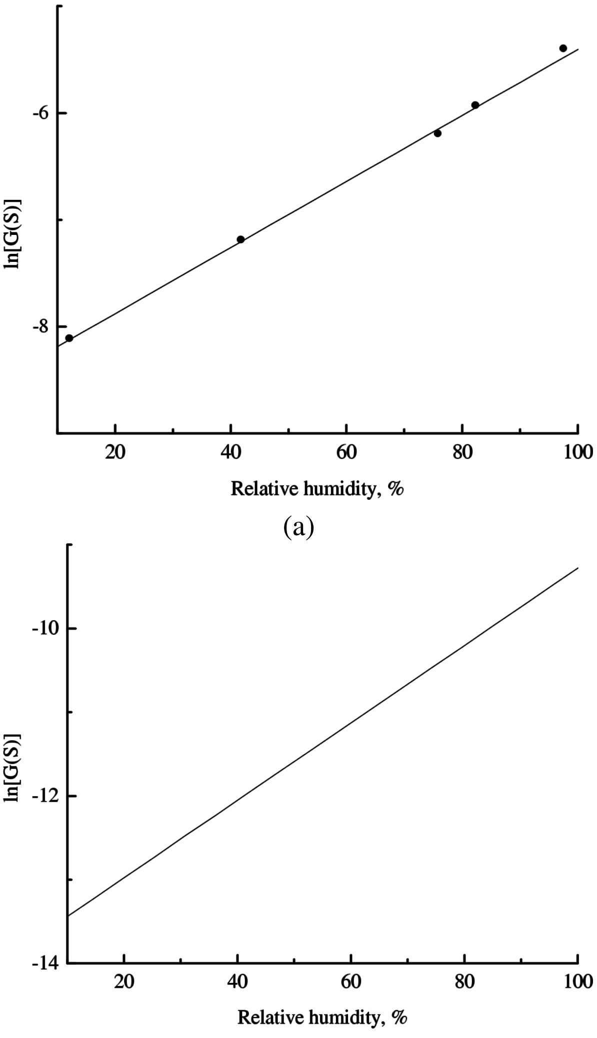


Fig. 7. Average conductivity dependences on the temperature of $M_2V_{12}O_{30.7}{\cdot}nH_2O$ (M = Li, K, Na) (curve *1*) and $MV_{12}O_{30.7}{\cdot}nH_2O$ (M = Mg, Ca, Sr, Ba) (curve *2*) xerogels [31, 32].

this case the jumps only between the nearest ions are taken into account. It is the so-called autolocalized (A) small polaron case [34]. If the concentration of the defects is less than the critical concentration of the metal–insulator transition, the additional electrons can be occupied and the bonded (B) polarons are formed [34]. The transition between autolocalized and bonded polarons occurs at the critical temperature T_K which can be determined from the equality of the electron jump probabilities (Eq. (7)) for A and B polarons [33]:

$$T_K = \frac{E_A - E_B}{2\alpha k R_{ii}(C^{-1/3} - 1)}, \qquad (10)$$

where E_A and E_B are the activation energies of the conductivity for A and B polarons, R_{ii} is the distance between the nearest ions, α is the decay of the wave function, and C is the reduction ratio of vanadium ions. Using the values $T_K \sim 350$ K, $E_A \sim 0.63$ eV, $E_B \sim 0.29$ eV (see Fig. 7), $R_{ii} = 2.43$ Å, and $C = 0.07$, from equation (10) one gets $\alpha = 1.97$ Å that corresponds to the α values for the transition metal oxide [35].



(a)

(b)

Fig. 8. Conductance dependences on the relative humidity for (a) $H_2V_{11}TiO_{30.3}{\cdot}nH_2O$ and (b) $H_2V_{11}\ MoO_{31.2}{\cdot}nH_2O$ (b) xerogels at 286 K [38].

3.1.5. Conductivity versus humidity

As mentioned in 3.1.1, the conductivity of hydrates consists of two components – electronic and ionic. The electronic part is determined by electron jumps between various valence vanadium ions and the ionic one is due to proton diffusion, while the ionic conductance depends upon the partial pressure of water [16]. Therefore it is clear that the total conductivity also depends on humidity conditions of the environment. The results of similar investigations are described in [36–43]. The dependences of the bulk conductance G on the relative humidity at 286 K are shown in Fig. 8 for $H_2V_{11}TiO_{30.3}{\cdot}nH_2O$ (Fig. 8(a)) and $H_2V_{11}MoO_{31.2}{\cdot}nH_2O$ (Fig. 8(b)) [37]. The experimental points of $\ln G = f(\varphi)$ (φ is the relative humidity) were fitted to a linear function

$$\ln G = a + b \cdot \varphi, \qquad (11)$$

where $a = -13.85 \pm 0.08$, $b = 0.045 \pm 0.001$ for $H_2V_{11}MoO_{31.2}{\cdot}nH_2O$ and $a = -8.42 \pm 0.21$, $b = 0.031 \pm 0.001$ for $H_2V_{11}TiO_{30.3}{\cdot}nH_2O$ xerogels. The sensitivities of the conductance, which are defined as

$$\beta = \frac{\mathrm{d}[\ln G]}{\mathrm{d}\varphi}, \qquad (12)$$

when T = const, are 0.045 (% RH)$^{-1}$ for V–Mo and 0.031 (% RH)$^{-1}$ for V–Ti xerogels [37–42].

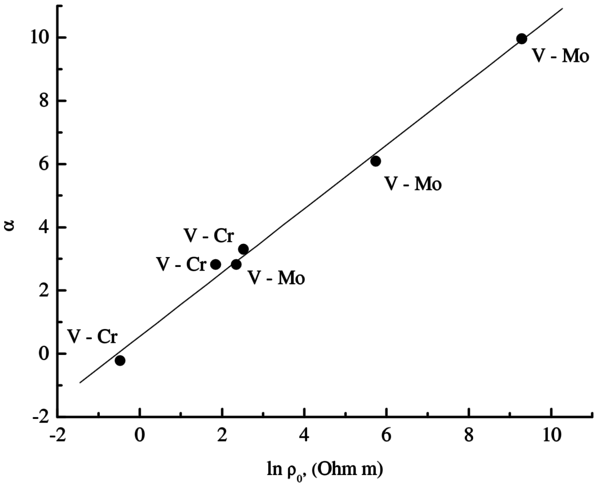


Fig. 9. Sensitivity α dependence on the oxide resistivity ln ρ_{ox} [43].

The bulk resistance of vanadium xerogels depends on the relative humidity φ as an exponential function [36–43]

$$\rho = \rho_0 \exp(-\alpha\varphi)\,, \qquad (13)$$

where ρ_0 (the resistivity at $\varphi = 0$) and sensitivity α are constants. Figure 9 shows the dependence of α on ρ_0 for $H_2V_{12-x}Mo_xO_{31\pm y}\cdot nH_2O$ and $H_2V_{12-x}Cr_xO_{31\pm y}\cdot nH_2O$ hydrates [43]. As shown in [43], the resistivity ρ_0 is connected with the electronic (ρ_{e}) and protonic (ρ_{p}) parts of the total resistivity and then the dependence of sensitivity α on ρ_{e} and ρ_{p} may be written as

$$\alpha = \ln\rho_{\mathrm{e}} - \ln\rho_{\mathrm{p}}\,. \qquad (14)$$

The electronic and protonic parts of the total conductivity have activation character with some activation energies ΔE_{e} and ΔE_{p}. The activation energy ΔE of the total conductivity depends on the relative humidity φ. As shown in [43], this dependence can be expressed through ΔE_{e} and ΔE_{p} as

$$\Delta E(\varphi) = \Delta E_{\mathrm{e}} + \varphi(\Delta E_{\mathrm{p}} - \Delta E_{\mathrm{e}})\,. \qquad (15)$$

The values of ΔE_{e} and ΔE_{p} for the $H_2V_{10}Cr_2O_{31.7}\cdot nH_2O$ are determined in [42] and they are 0.22 ± 0.01 eV and 0.31 ± 0.02 eV respectively.

3.1.6. Switching phenomenon

The experimental results of investigation of the switching phenomenon in thin layers of the vanadium pentoxide based xerogels are presented in [44, 45]. The typical switching characteristic of $H_2V_{12}O_{30.7}\cdot nH_2O$ xerogel is shown in Fig. 10 [45]. Upon applying some critical voltage U_1, named switching voltage, the conductivity of a sample sharply increases, therefore the voltage jump decreases down to the value U_2 and the current through the sample simultaneously grows. It is necessary to note that this characteristic is observed only after a primary forming of the sample by appplying a voltage pulse with a capacity of the order of 0.1 J. Without the primary forming the voltage–current characteristic is linear when the electric field of strength up to 10^2 V/m is applied, and afterwards the deviation from linearity is observed that is caused by the Joule heating. At raising the environment temperature the switching voltage declines and upon achieving the temperature $T > 336$ K the phenomenon of switching is not observed. Disappearance of switching at 336 K allows one to assume that the impurity vanadium dioxide, which is formed as a result of the electrical forming of the sample, is responsible for the switching phenomenon in xerogels [45].

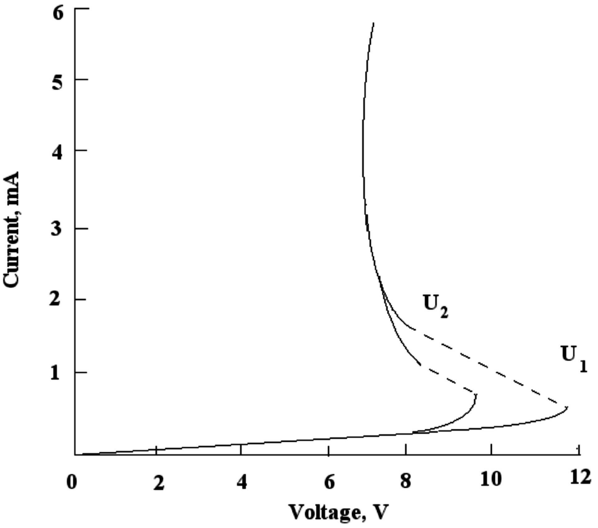


Fig. 10. Switching characteristic of $H_2V_{12}O_{30.7}\cdot nH_2O$ xerogel after electrical forming [45].

4. X-ray photoelectron spectra

Research results of X-ray photoelectron spectra of xerogels are described in [46–54]. It is known that this method allows determining the valence states of ions. It is established that partial dehydration of xerogels, reduction of oxygen, and lower valence metal ions occur after bombardment of the xerogels by argon ions. In Table 3 the results of changes of the concentration and valences depending on the bombardment duration are presented for $M^{II}V_{12}O_{30.7}\cdot nH_2O$ (M^{II} = Ba, Sr, Ca, Mg), $M^{I}_2V_{10}Mo_2O_{31.7}\cdot nH_2O$ (M^{I} = K, Na, Li), and $H_2V_{11}TiO_{30.3}\cdot nH_2O$ xerogels [49–54]. As follows from the table, after 30 seconds of bombardment, in all compounds alongside with ions of

Table 3. Changes of concentrations of various ions in xerogels during bombardment by Ar^+ ions.

Xerogel	Ion	Duration of bombardment (min.)				
		0	0.5	2	5	10
$\mathrm{M^{II}V_{12}O_{30.7}\cdot}n\mathrm{H_2O}$	V^{5+}	89 at.%	57 at.%	41 at.%	36 at.%	35 at.%
	V^{4+}	11 at.%	40 at.%	50 at.%	49 at.%	50 at.%
	V^{3+}	0 at.%	3 at.%	9 at.%	15 at.%	15 at.%
$\mathrm{M^{I}_2V_{10}Mo_2O_{31.7}\cdot}n\mathrm{H_2O}$	V^{5+}	95 at.%	78 at.%	61 at.%	58 at.%	55 at.%
	V^{4+}	5 at.%	18 at.%	32 at.%	33 at.%	35 at.%
	V^{3+}	0 at.%	4 at.%	7 at.%	9 at.%	10 at.%
	Mo^{6+}	100 at.%	95 at.%	76 at.%	70 at.%	67 at.%
	Mo^{4+}	0 at.%	5 at.%	24 at.%	30 at.%	33 at.%
$\mathrm{H_2V_{11}TiO_{30.3}\cdot}n\mathrm{H_2O}$	V^{5+}	86 at.%	67 at.%	53 at.%	38 at.%	38 at.%
	V^{4+}	14 at.%	30 at.%	38 at.%	48 at.%	48 at.%
	V^{3+}	0 at.%	3 at.%	9 at.%	14 at.%	14 at.%
	Ti^{4+}	100 at.%	100 at.%	100 at.%	100 at.%	100 at.%

Table 4. Reduction of the oxygen concentration in xerogels after 10 min bombardment by Ar^+ ions.

Xerogel	$-\Delta$O, %
$\mathrm{M^{II}V_{12}O_{30.7}\cdot}n\mathrm{H_2O}$	13
$\mathrm{M^{I}_2V_{10}Mo_2O_{31.7}\cdot}n\mathrm{H_2O}$	22
$\mathrm{H_2V_{11}TiO_{30.3}\cdot}n\mathrm{H_2O}$	24

vanadium of valence four and five the V^{3+} or V^{4+} ions are formed alongside with molybdenum of valence six. Thus their concentration increases with duration of bombardment and after 10 minutes tends to saturation. It is accompanied by a reduction of oxygen in the samples that is presented in Table 4. From Table 3 the reduction ratio of xerogels concentration $C = C_{\mathrm{V}^{4+}}/(C_{\mathrm{V}^{4+}} + C_{\mathrm{V}^{5+}})$ at the moment of time $t = 0$ is equal to 0.05 for $\mathrm{M^{I}_2V_{10}Mo_2O_{31.7}\cdot}n\mathrm{H_2O}$, to 0.11 for $\mathrm{M^{II}V_{12}O_{30.7}\cdot}n\mathrm{H_2O}$, and to 0.14 for $\mathrm{H_2V_{11}TiO_{30.3}\cdot}n\mathrm{H_2O}$ xerogels. This should support that the conductivity of the specified groups of compounds should increase with the growth of quantity C, and that appears to be a true result [55]. From all the investigated xerogels on the basis of vanadium pentoxide the greatest reduction ratio $C_{\mathrm{V}^{4+}}/(C_{\mathrm{V}^{4+}} + C_{\mathrm{V}^{5+}}) = 0.24$ and consequently also the greatest conductivity possess the hydrates of V_2O_5 containing up to 9.5 mole % of GeO_2 [56].

5. Conclusions

The gels on the basis of polyvanadic acids possess unique physical properties which are possible to adjust over a wide range that allows one to find for them lots of applications in various areas of technology. On the basis of vanadium oxide gels the $\mathrm{TTF}_x\mathrm{V_2O_5}$ and Bz_x–$\mathrm{V_2O_5}$ (Bz is benzidine, $x \geq 1$) compounds are produced, which are the first molecular bronzes of transitional metal oxides [57]. The electric conductivity of the last one at room temperature equals $2.8\cdot10^8$ S/m. Moreover, nanotubes on the basis of vanadium pentoxide have been synthesized rather recently by using the sol–gel technology [58–60].

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HIDRATUOTŲ VANADŽIO JUNGINIŲ ELEKTRINĖS SAVYBĖS

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Santrauka

Vanadžio pentoksido geliai turi sluoksniuotą sandarą, kur V–O sluoksniai atskirti vandens molekulėmis. Tai leidžia įterpti tarp sluoksnių įvairius jonus bei molekules. Elektrinis gelių laidumas turi du sandus – elektroninį, atsirandantį dėl elektronų šuolių tarp įvairiavalenčių jonų, ir protoninį, kurį lemia protonų difuzija.

Pateikti hidratuotų vanadžio junginių, tokių kaip $\mathrm{H_2V_{12-\mathit{x}}Me_\mathit{x}O_{31\pm\delta}}\cdot n\mathrm{H_2O}$ (Me = Mo, Ti, Cr), $\mathrm{Me_2V_{12}O_{31\pm\delta}}\cdot n\mathrm{H_2O}$ (Me = Li, Na, K, Rb, Cs) ir $\mathrm{MeV_{12}O_{31\pm\delta}}\cdot n\mathrm{H_2O}$ (Me = Mg, Ca, Ba), kompleksinių tyrimų rezultatai.

Pagrindinis dėmesys skirtas hidratų sandaros, sintezės, elektrinių savybių ypatybėms ir metalų jonų valentingumui.