Proton transfer in $V_2O_5$–$P_2O_5$ glasses

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Abstract. Proton transfer in porous $V_2O_5$–$P_2O_5$ glasses is shown for the first time using measurements of electrical conductivity as a function of air humidity. The materials under consideration are characterized by reversible physical sorption of water at temperatures below 100 °C, during which the conductivity decreases. Irreversible chemisorption of water is observed at 150 °C, which leads to the appearance of proton transfer.

1. Introduction
Proton-conducting oxide glasses have been known for about 55 years, and such studies started after the work of H. Nakamura and Y. Asahara, where the charge transfer in barium phosphate glasses was suggested to be protonic [1]. Based on the Nakamura’s suggestion, Japanese scientists leading by Y. Abe presented a number of researches aimed at the study of the nature of proton conductivity in metal-phosphate glasses [2-7], suggested using porous glasses for proton conductivity studies [4], and proposed the first model of proton conductivity in glasses [7]. A great contribution to the investigation of proton-conducting glasses was also made by research groups leading by M. Nogami [8-12] and T. Uma [13-15], who studied silica phosphate glasses and worked together. The leaders of these groups presented a low-temperature fuel cell with PWA/PMA–$P_2O_5$–SiO$_2$ glass composite membrane (PWA–phosphotungstic acid and PMA –phosphomolybdic acid) [16].

$V_2O_5$-containing glasses are promising for electrochemical applications because of their high conductivity compared to other electron-conducting glasses. There are numerous works devoted to the study of their structure and properties, especially for vanadate-phosphate systems [17-20]. In our opinion, in addition to the electronic conductivity, $V_2O_5$-containing glasses might also have protonic conductivity like crystalline vanadium oxides. It is known that the electronic structure of crystalline vanadium oxides is sensitive to ambient gaseous media of different chemical nature. Due to this, nanostructures based on vanadium oxides VOs are widely used to create resistive sensors for various gases [21]. In particular, they are used as sensors for molecular hydrogen [22, 23] and humidity [24, 25], as well as for creating a two-dimensional proton pump [26]. At the same time, glassy vanadium oxides have not been studied at all in this vein despite the fact that such glasses could be used as IT-gas sensors. To the best of our knowledge, this work presents the first study of the possibility of proton transfer in vanadate-phosphate glasses.

2. Experimental
Glasses in $xP_2O_5$–(100–$x$)$V_2O_5$ ($x = 10$ and 15 mol%); the compositions are assigned as VP10 and VP15, respectively) system were obtained by conventional melt-quenching technique. Appropriate
amounts of vanadium oxide and ammonium dihydrogen phosphate were mixed thoroughly in a jasper mortar; the obtained mixture was put into a platinum crucible, heated to 900 °C, and held for 1 h. After synthesis, the samples were annealed at a temperature of \(T_g-50\ °C\).

Elemental analysis of the synthesized samples was carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an instrument OPTIMA 4300 DV (Perkin Elmer, USA). The degree of amorphousness of the obtained glasses was checked by X-ray diffraction (XRD) analysis on a D/Max-2200VL/PC (Rigaku, Japan) in Cu-K\(\alpha\) radiation. The measurements were carried out at room temperature in the range of \(2\theta = 10° - 70°\).

The powdered samples were pressed using a PLG-20 uniaxial press (LabTools, Russia) at a pressure of 70 MPa. The compacts were sintered at 200 °C for 20 minutes in air. The specific surface area of the compacts was determined by the Brunauer–Emmett–Teller (BET) method. The compacts were divided into granules and nitrogen sorption-desorption was performed using a Sorby N4.1 equipment (Meta, Russia). Optical micrographs of the compacts were carried out with a MIM-7 metallographic microscope (LOMO, Russia) in the dark field mode.

The electrical conductivity of the compacts was studied by electrochemical impedance spectroscopy (EIS) using the SP-200 platform (BioLogic, France). The compacts were clamped between two platinum pads. The measurements were carried out in the frequency range from 7 MHz to 500 mHz with a sinus amplitude of 100 mV. Before measuring the electrical conductivity, the samples were dried at a temperature of 150 °C by blowing dry air through the measuring system, the air was dried by using a column with zeolites. The atmospheric humidity was controlled by bubbling air through a vessel with water, thermostated at temperatures in the range of 0 – 44 °C. In this case, the partial pressure of water vapor (pH\(\text{H}_2\text{O}\)) varied in the range of 0.6 – 9.1 kPa according to the phase diagram of water.

3. Results and discussion
Properties of VP10 and VP15 glasses were earlier studied by us in [20]. It was shown that the content of vanadium and phosphorus in samples VP10 and VP15 according to the ICP-AES analysis results corresponds to the ratio specified in the synthesis. XRD analysis results confirm the amorphous state of the materials with no signs of crystalline phases. Optical micrographs of VP10 and VP15 compacts, shown in Figure 1, demonstrate the porous microstructure of the samples with macropores, which provides good gas access to the surface of the materials. The specific surface area according to the BET analysis was 0.87 ± 0.02 m\(^2\)/g and 0.67 ± 0.05 m\(^2\)/g for the VP10 and VP15 compacts, respectively.

![Figure 1. Optical micrographs of compacts VP10 (a) and VP15 (b).](image)

Figure 2 shows the dependences of the conductivity in Arrhenius coordinates for dense and porous samples VP10 and VP15 in a dry air atmosphere. Unfortunately, the determination of the density of compacts is complicated by the chemical reactivity of the materials. For example, measurement by the Archimedes method is impossible due to the active dissolution of materials in various liquids. Nevertheless, by comparing the conductivity of dense and porous samples, it is possible to evaluate the effect of porosity on conductivity. Despite the difference in the conductivity of about half an order of magnitude between dense and porous samples, we can see comparable values of the activation
energies of conductivity, which are about 35-38 kJ/mol. These values mainly reflect the electron transfer in the studied glasses [20].

In the context of studying proton transfer, an important property is the surface area that can interact with water vapor. It was shown that dense samples are insensitive to humidity, which confirms that the transfer of protons in such systems is possible only over the surface of the material. For porous compacts at temperatures of 50 ºС and 100 ºС, the conductivity of both VP10 and VP15 compacts decreases with increasing air humidity (Figure 3).

The dependence of the conductivity of materials on the partial pressure of water vapor (pH₂O) is well described within the framework of the laws of physical sorption, for example, Langmuir’s law. The dependences in Figure 3 are linear in the coordinates \( \log(\sigma) = f(\log(p\text{H}_2\text{O})) \).

Physical sorption is also indicated by the fact that sorption-desorption processes are reversible, since the conductivity of materials changes reversibly with a change in air humidity. A similar dependence on the humidity in accordance with Langmuir's law for crystalline phases VOₓ was observed in [25] in a wide temperature range. The decrease in conductivity during the adsorption of oxygen-containing molecules is usually explained by a decrease in the concentration of n-type electrons on the vanadium oxide surface due to the dipole interaction [22, 23].

Figure 2. Temperature dependencies of the total conductivity of porous (points) and dense (lines) samples VP10 and VP15 in a dry air.

Figure 3. Dependencies of the total conductivity of VP10 (a,c) and VP15 (b,d) compacts on air humidity at 50 ºС and 100 ºС.
Unlike temperatures of 50 ºС and 100 ºС, at 150 ºС the process of irreversible chemisorption of water vapor is observed. The transition from physically adsorbed water to chemisorbed water with increasing temperature is justified by an increase in the adsorption enthalpy [27]. The conductivity of VP10 and VP15 compacts increases with an increase in the partial pressure of water vapor, as seen in Figure 4. It can be concluded that the increase in the conductivity of the samples with increasing humidity is associated with the contribution of the proton conductivity. This fact is confirmed by the strictly linear dependence of the total conductivity on pH$_{2}$O$^{1/2}$. In general case [27, 28], proton charge carriers in oxides are formed in accordance with the hydration equation (Kröger–Vink notation):

$$H_2O + X_0^{**} + O_0^X \rightarrow 2OH_0^*$$

(1)

where two proton defects $OH_0^*$ arise when a water molecule interacts with adsorption center $X_0^{**}$ on the oxide surface (e.g. oxygen vacancy) and the neighboring oxygen atom $O_0^*$ from the oxide.

The mechanism of proton transfer in glasses [7] assumes that water molecules are incorporated into oxygen polyhedra to form OH groups, and protons are transferred by jumping over oxygen atoms by the Grotthuss mechanism. In particular, this behavior has been shown for phosphate glasses [29, 30]. Embedding in the structure of phosphate glass, a water molecule breaks the P–O–P bond with the formation of two P–OH groups. VO$_4$ tetrahedrons in glasses have a similar structure to PO$_4$ tetrahedrons [31]. Thus, we can expect that the mechanism of proton transfer through VO$_4$ tetrahedrons is similar.

![Figure 4](image)

**Figure 4.** Dependencies of the total conductivity on air humidity of VP10 (a) and VP15 (b) and dependence of proton conductivity of VP10 and VP15 (c) at a temperature of 150 ºС.

The values of the proton conductivity of the VP10 and VP15 materials were obtained by subtracting the conductivity in extremely dry conditions at pH$_2$O = 0 Pa from the total conductivity. Conductivity under extremely dry conditions was obtained by linear approximation of the dependence $\sigma = f(pH_2O^{1/2})$. In Figure 4c, one can see that the proton conductivity of materials is linear with pH$_2$O$^{1/2}$. The samples are close to saturation with water vapor at pH$_2$O = 9.1 kPa. Sample VP10 exhibits slightly higher proton conductivity than sample VP15. Most likely, the difference in proton conductivity is due to the difference in the specific surface of the samples. It should be noted that the
hydration of samples VP10 and VP15 at a temperature of 150 °C is irreversible. Therefore, strictly speaking, the dependences shown in Figure 4 are not a function of the partial pressure of water vapor, but a function of the concentration of chemisorbed water on the surface of materials.

Figure 5 shows the XRD patterns of samples VP10 and VP15 before and after measurements in a humid atmosphere at 150 °C. It is seen that the chemisorption of water does not lead to the crystallization process in the samples. XRD curves of samples after measurements were collected from the compact surface, so their shape is slightly different.

4. Conclusion
The effect of humidity on the conductivity of phosphate-vanadate glasses was studied. The conductivity behavior of these glasses strongly depends on temperature and humidity. At the temperature of 100°C and below, conductivity decreases in logarithm coordinates with increasing the air humidity that seems like Langmuir's law indicating physical sorption of water. This is confirmed by the reversibility of the process.

At a temperature of 150°C, the character of interaction changes dramatically, and conductivity grows linearly on pH2O1/2 which agrees with quasi-chemical representations about the formation of proton carriers in materials. The growth of conductivity ion, in this case, is explained by the contribution of proton conductivity. The saturation of glass with protons at this temperature is irreversible which indicates the chemical bonding of water with the material.

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