Structure-conductivity correlation in $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ glass for low-temperature SOFCs

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This article focuses at searching of a direct relationship between composition and structure, on one hand and electrochemical behavior (conductivity), on the other hand of transition metal oxide system. Bulk sample with composition $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ has been synthesized by means of melt quenching method. The XRD diffraction study has defined the amorphous nature of the sample; the structure determined by IR technique displays presence of VO_5 groups and isolated PO_4^{3-} (Q^0) structural units. The sample possesses both proton and oxide ion conductivities registered by electrochemical impedance spectroscopy. The observed change in the impedance behavior at 350 ºC in hydrogen atmosphere is related to the intrinsic transformation from glass to crystalline state.

INTRODUCTION

Economically competitive solid oxide fuel cells (SOFC) appear suited for commercialization but widespread market penetration requires continuous innovation of materials and fabrication processes to enhance system lifetime and reduce costs. An effective approach to cost reduction is the lowering of the operating temperature without inferring performance losses and improvement in the cell architecture and technology [1]. This can be achieved through several ways. One approach is decrease of the active layers thickness. For electrolyte 5 µm is already a realistic dimension in respect to technological realization [1]. Another pathway is the introduction of new architectures, such as composite cathodes based on a mixture of electrode and electrolyte material [1] or new designs An important achievement is the development of the proton conducting fuel cell (PCFC), where the more mobile protons are transported through the electrolyte, which reduces the operating temperature.Recently an innovative concept, called dual membrane fuel cell (dmFC) was introduced [2-3]. It combines the advantages and bypasses the disadvantages of both SOFC and PCFC in respect to the effect of the water, introducing a separate chamber for its formation and evacuation. This design is connected to the application of materials with mixed ionic (protonic and oxide ion) conductivity. The most promising approach in SOFC optimization is the development of new materials with high conductivity at lower operating temperatures. The current target is 600-500 ºC.

The traditional electrolytic material in SOFCs - Yttrium-stabilized zirconium oxide YSZ which has high oxide conductivity and high stability in both oxygen and in reduction atmosphere [4] is replaced most often with (i) Cerium oxide CeO_2doped with CaO, Y_2O_3 and rear earth oxides such as Gd_2O_3[5], (ii) SrO- and MgO-doped Lanthanum galalate $LaGaO_3$ [6].

However, the challenge is to decrease additionally the operating temperature, filling the gap between SOFC and PCFC with polymeric membrane which is the range between 200-400 ºC. In this direction a good strategy for development of new proton conducting materials with high proton conductivity is the introduction of cation-off stoichiometric materials. The charge imbalance caused by the cation non-stoichiometry is compensated by protons. Phosphates are among the materials that receive much attention due to the high thermal conductivity [6]. Depolymerization of the phosphate network and incorporation of transition metal ions, such as vanadium, produces new pathways for proton mobility by modification and deformation of the crystal structure. Furthermore, transition metals, when combined with other elements, can form compounds with various chemical bonding: ionic (oxides), covalent (sulfides, arsenide), metallic (carbides, nitrides).

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Vanadate glasses contain V^{4+} and V^{5+} ions where the electrical conduction is facilitate to the hopping of 3_{d1} unpaired electron from V^{4+} to V^{5+} sites. Vanadate glasses have been considered as a new branch in semiconducting glasses because of their wider glass-forming region and possible technological applications [1].

The Electrochemical Impedance spectroscopy is a powerful technique to reveal underlying chemical processes as a response of the applied small perturbation signal. The strength of EIS originates from its capability to differentiate the steps comprising the overall electrochemical process and to supply detailed information about the surface and the bulk properties of various electrochemical systems [7].

This article focuses at searching of a direct relationship between composition and structure, on one hand and electrochemical behavior (conductivity), on the other hand of transition metal oxide system. Having into account the observed mixed ionic conductivity obtained in some proton conducting ceramic electrolytes for PCFC [8], in addition to the proton conductivity studies,investigation for oxide ion conductivity were also performed.

This work presents study of relationship between structure of the materials and conductivity of mixed $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ glassin view of their potential use as electrolytes in SOFCs.

EXPERIMENTAL

A bulk glass with composition $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ was synthesized by means of melt quenching method. The homogenized mixture of initial materials: TiO_2 and V_2O_5 powders and orthophosphoric acid H_3PO_4,were loaded in a quartz crucible. The heating process was carried out in a furnace gradually increasing the temperature upto 1000°C. The glass was obtained by quenching between two pre-cooled copper plates.

The phase formation of the sample was investigated by X-ray diffraction (XRD) method by means of X-ray diffractometer Philips APD-15. The data were collected with a constant rate of 0.02 deg.s⁻¹ over an angle range $2\theta = 20°\div70°$ using CuK_α radiation ($\lambda = 1.54178$ Å) at ambient temperature.

Fourrier Transformed Infrared (FTIR) spectrum was recorded with a FTIR spectrometer model VARIAN 660-IR in the frequency range 400 – 1300cm⁻¹. The data were collectedwith a resolution of 2 cm⁻¹ at room temperature.

The impedance measurements were performed on polished sample with Ag electrodes in hydrogen and air atmosphere. The experiments were carried out on Solartron 1260 FRA in temperature interval 25°C–350 °C, frequency range from 1 MHz down to 0.1 Hz, density of 5 points/decade.

The differential thermal analysis (DTA) and the thermogravimetric analysis (TGA) analyses were performed on SeteramDTA/TGlabSysevo 1600 technique in temperature range between 25°C and 800°C in air at heating rate of 10°C/min in platinum crucible.

RESULTS AND DISCUSSION

X-ray Diffraction investigation

The investigated sample is considered as roentgenographically amorphous. The spectrum is characterized by a broad hallo and absence of crystalline peaksas seen from the XRD analysis (Fig. 1).
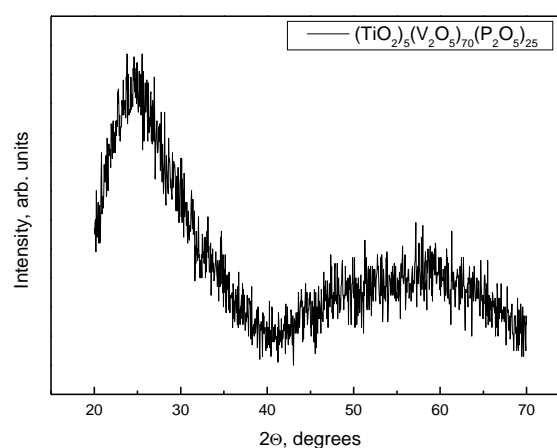

Fig. 1. XR-diffractogram of $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ glass.

Infrared spectroscopy study.

The infrared spectrum presented in fig. 2 is analyzed by using the Tatre and Condrate empirical method. According to this approach, one can compare the glass spectra with their crystalline counterparts. Similarity of the spectra in the two solid states is considered as confirmation for existence of resemblance in the type and the symmetry of the building structural units. The interpretation is based on the following observations: (1) the glasses have a local symmetry of the separate molecular groups; (2) the intermolecular vibrations are less intensive than those between the groups due to the absence of long range order.

Phosphate glasses might be analyzed as a polymeric network of tetrahedra composed of $[PO_4]$ groups.The structure is usually described by Q^n, where *n* stands for the number of bridged oxygen atoms in a tetrahedron and different structures can

be formed depending on the [O]/[P] ratio: the Q^3 tetrahedra form network, while Q^2 tetrahedra are arranged in polymeric metaphosphoric chains with $(PO_2)^-$bond. "Inverted" glasses are based on pyro (Q^1) with a structural unit of $(PO_3)^{2-}$ groups [9-11].

The absorption band at 1020 cm^{-1} most probably is a superposition of overlapping peaks. It is due to VO_5 deformated trigonal bipyramids with vanadium ion in the center and short V=O (vanadyl) bond. The addition of modificator (phosphorus) introduces non-bridged oxygen atoms in the glass and leads to depolymerization of the phosphate network. The oxygen atoms destroy the P-O-P bridge structure [10-12] forming isolated phosphate groups (short chains and pyrophosphate groups). The absorption at 1020 cm^{-1}indicates the presence of these groups.
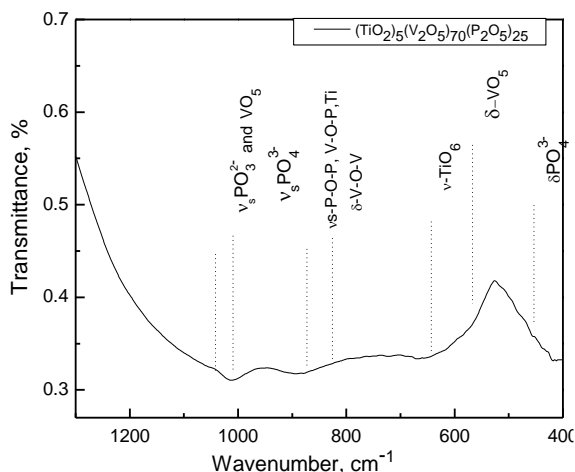

Fig. 2. Infrared spectra of $(TiO_2)_x(V_2O_5)_y(P_2O_5)_{100-x-y}$ glassy system.

The 900 cm^{-1}mode is assigned to the mixed V-O-Pbonds. The band suited between 838 – 820 cm^{-1} arises from V-O-V bending, while bending vibrations of VO_5-groups are found below 600cm^{-1}. The characteristic absorptions of VO_4 bands are located in the 980 –820 cm^{-1}range. The vibrational modes located at around 640 cm^{-1} belong to TiO_6 octahedral structures that define the structure of titanium oxides [13].

Conductivity studies by Electrochemical Impedance Spectroscopy.

Two impedance spectra of the sample measured in both oxygen and hydrogen atmosphere at 250 ºC are represented in fig. 3.

The low-frequency semicircles are well-defined and describe the behavior of the electrode reaction. There is a strong deformation in air, i.e. strong frequency distribution arising from the changes that are commented below (fig. 5). The high frequency part corresponds to the electrolyte reaction with a

resistance that can be easily evaluated: 350Ω in hydrogen atmosphere and 290 Ω in air. Since the sample is amorphous, the electrolyte resistance should be related only to the bulk material. The results show that at 250 ºC the sample possesses mixed oxide and proton conductivity and the oxide one is higher.

A possible explanation of this phenomenon is the existence of oxygen vacancies which are needed for the activation of the proton conductivity [14]. Obviously, their concentration, according to eq. 1 [14], is high enough to introduce good oxide ion conductivity.
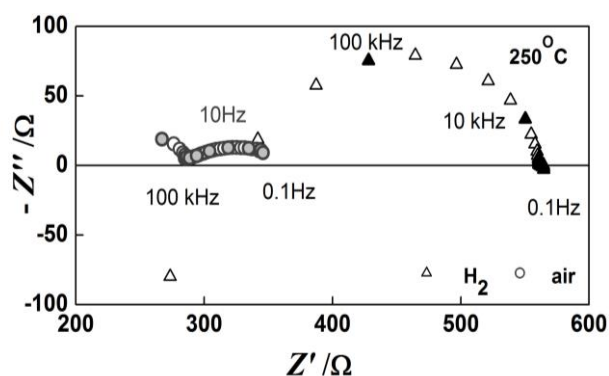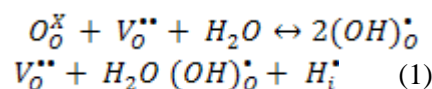
$$O_O^x + V_O^{\bullet\bullet} + H_2O \leftrightarrow 2(OH)_O^{\bullet}$$
$$V_O^{\bullet\bullet} + H_2O (OH)_O^{\bullet} + H_i^{\bullet} \qquad (1)$$

Fig. 3. Impedance diagram of $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ composition in both air (at 178 min) and hydrogen atmospheres at 250 ºC.

Additional phenomenon is observed in air atmosphere at 250 ºC where the sample resistance decreases from 430 Ω to 260 Ω (fig. 5). As a consequence of this decrease, the resistance values of the material in air and hydrogen atmospheres become similar in the temperature range 250-350ºC. This is evident from the Arrhenius plots in air and hydrogen atmospheres, displayed in fig. 6.
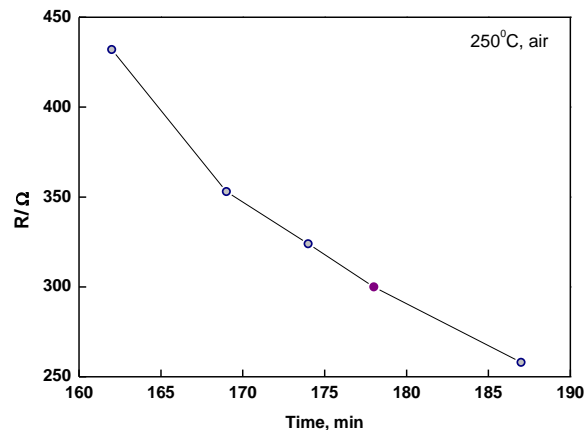

Fig. 5. Resistance change of $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ sample with time in air.

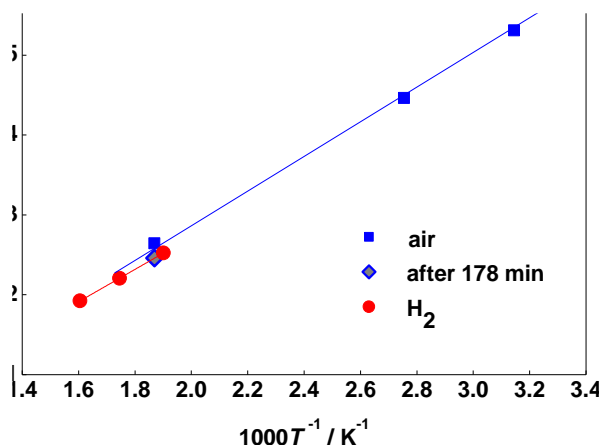**Fig. 6.** Bulk Arrhenius plots of $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ in air and hydrogen.

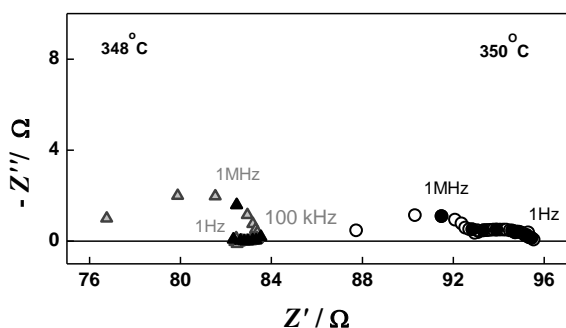**Fig. 7.** Impedance spectrum of $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ glass at 350 ºC (measured first) and at 348 ºC measured 2 min after the first one.

In hydrogen the sample follows the temperature trend shown in fig. 6. At 350 ºC an abrupt change in the impedance behavior (including the value of the resistance) is clearly seen in fig. 7.
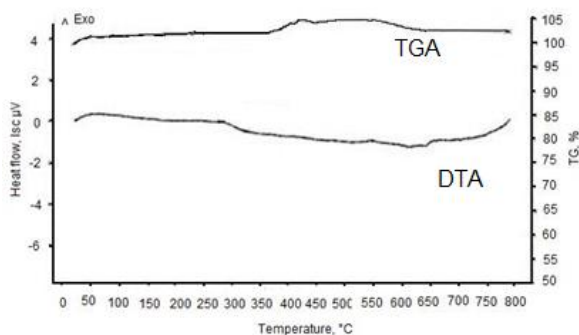

Fig. 8. DTA/TG analysis of $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ glass.

The performed DTA/TG analysis (Fig. 8) shows that 350 ºC marks exactly the beginning of glass transition temperature, i.e. the temperature region where transformation of the intrinsic nature of the material occurs and therefore, where a change in the electrochemical impedance behavior has been

detected. Obviously, the impedance diagram shown in fig. 7 at 348 ºC registers exactly the transformation in the state.

CONCLUSIONS

The bulk material with composition $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ synthesized and characterized by means of XRD diffraction and IR techniques has been found roentgenographically amorphous. The structure of the glass studied by IR analysis indicated presence of VO_5 groups and isolated $PO_4^{3-}(Q^0)$.EIS investigation shows that the material possesses proton and oxide ion conductivities. We observed a change in the impedance spectrum at intermediate temperatures whichis due tointrinsic transformation during the heating of the material of the $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$.

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ЗАВИСИМОСТ МЕЖДУ СТРУКТУРА И ПРОВОДИМОСТ НА $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ ЗА НИСКОТЕМПЕРАТУРНИ ТОГК

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(Резюме)

Този труд е фокусиран върху търсенето на директна взаимовръзка между състав и структура, от една страна, и електрохимичното поведение (проводимост), от друга, на $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ стъклообразен материал за приложение в нискотемпературни твърдотелни оксидни горивни клетки (ТОГК).

Синтезиран е обемен образец със състав $(TiO_2)_5(V_2O_5)_{70}(P_2O_5)_{25}$ по метода на застъкляване от стопилка. Проведеният рентгено-структурен анализ потвърждава аморфната природа на пробата; изследването на структурата чрез инфрачервена спектроскопия показва наличие на VO_5 групи и изолирани PO_4^{3-} (Q^0) структурни единици. Пробата проявява едновременно протонна и кислородна проводимост, регистрирана чрез електрохимична импедансна спектроскопия. Наблюдаваната промяна в импедансното поведение при 350 ºC във водородна атмосфера се отдава на превръщането на аморфния материал в кристален.