

# A XANES study of the valence state of vanadium in lithium vanadate phosphate glasses

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Valence states of vanadium in  $\text{Li}_2\text{O-V}_2\text{O}_5\text{-P}_2\text{O}_5$  electronic-ionic conducting glasses have been studied by X-ray absorption spectroscopy. The composition dependence of the XANES range of the spectra has been used to estimate relative abundance of the vanadium atoms in  $\text{V}^{4+}$  or  $\text{V}^{5+}$  charge states. This information is important for analysis of electronic transport in these glasses, which occurs via electronic hopping between aliovalent vanadium centers. It was found that in samples with the lowest  $\text{V}_2\text{O}_5$  contents (10 mole% of  $\text{V}_2\text{O}_5$ ) a vast majority of vanadium ions are in  $\text{V}^{4+}$  charge state. At higher  $\text{V}_2\text{O}_5$  contents the proportion of  $\text{V}^{4+}$  ions decreases at the expense of  $\text{V}^{5+}$  ones, but remains substantial even in glasses with the highest contents of  $\text{V}_2\text{O}_5$ . © 2005 Springer Science + Business Media, Inc.

## 1. Introduction

Depending on the composition,  $\text{Li}_2\text{O-V}_2\text{O}_5\text{-P}_2\text{O}_5$  glasses exhibit purely ionic, mixed ionic-electronic or purely electronic conduction [1, 2]. Therefore they can be potentially used in e.g. lithium microbatteries as either electrolytes (ionically conducting compositions) or electrodes (mixed electronically-ionically conducting glasses). Ionic conduction in these glasses occurs via transport of  $\text{Li}^+$  ions, while electronic transport consists in the electron (small polaron) hopping between aliovalent  $\text{V}^{4+}$  and  $\text{V}^{5+}$  centers present in vanadate glasses.

Our recent conductivity measurements [1, 3] indicated that glasses with high amount of  $\text{V}_2\text{O}_5$  exhibit predominantly electronic conduction (due to a large concentration of  $\text{V}^{4+}/\text{V}^{5+}$  pairs in such glasses). Glasses with low vanadate contents (and high amounts of  $\text{Li}_2\text{O}$ ) are predominantly ionic conductors (because of high concentration of  $\text{Li}^+$  ions from the  $\text{Li}_2\text{O}$  modifier). In glasses of intermediate compositions we observed mixed electronic-ionic conduction.

Local structure of the glasses and the occupancy of valence states of vanadium belong to key factors influencing electric charge transport phenomena. Early studies [4, 5] on binary  $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$  glasses, based on EPR studies and wet chemical analyses, indicated that the relative abundance of vanadium in  $\text{V}^{4+}$  valence state ( $c = [\text{V}^{4+}]/([\text{V}^{5+}] + [\text{V}^{4+}])$ ) is a decreasing function of  $\text{V}_2\text{O}_5$  content in a glass. It was also reported that  $\text{V}^{5+}$  ions in as-received  $\text{V}_2\text{O}_5$  xerogels are partially reduced to  $\text{V}^{4+}$  or even to  $\text{V}^{3+}$  upon lithium intercalation [6]. Many papers, e.g. [7–10] addressed the problem of vanadium ion coordination in vanadate glasses

with various additives. Four-, five- or six-fold coordination by oxygen ions were proposed, depending on glass composition, however the issue still needs more investigations. An important conclusion based on studies carried out to-date is that in  $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$  glasses each apex oxygen of a  $\text{VO}_5$  unit belongs to a  $\text{PO}_4$  unit [11].

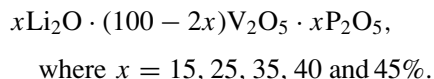
In this work we present the results of our XANES (X-Ray Absorption Near Edge Structure) studies done in order to estimate relative occupancy of valence states of vanadium in lithium vanadate phosphate glasses. The XANES experiments were done using the synchrotron radiation near the K-edge of vanadium. Additionally we measured full EXAFS (Extended X-Ray Absorption Fine Structure) spectra of these glasses. The compositions of the selected series corresponded to different values of the modifier-to-network former ratio  $r = [\text{Li}_2\text{O}]/([\text{V}_2\text{O}_5] + [\text{P}_2\text{O}_5])$ . This parameter is an adequate measure of disruption of the glass network (built by  $\text{V}_2\text{O}_5$  and  $\text{P}_2\text{O}_5$ ) by a modifier ( $\text{Li}_2\text{O}$ ). It means that for higher values of  $r$  the glass network, consisting of vanadate and phosphate polyhedra is more disrupted. In such cases the electronic conduction paths are discontinuous and the network is more open for transport of  $\text{Li}^+$  ions.

## 2. Experimental

Glasses were prepared by a standard melt-quenching method [1, 3]. Reagent grade chemicals:  $\text{LiNO}_3$  (Aldrich),  $\text{V}_2\text{O}_5$  (ABCR) and  $\text{NH}_4\text{H}_2\text{PO}_4$  (POCh), were used in the syntheses. A series of

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compositions described by the following formula was prepared:



For compositions containing 10, 20, 30, 50, 70%  $\text{V}_2\text{O}_5$ , the parameter  $r$  decreases from 0.82 through 0.67, 0.54, 0.33 to 0.18 respectively. XRD measurements showed no presence of crystalline phases in the prepared samples.

Measurements of X-ray absorption spectra were performed at HASYLAB in Hamburg. Glasses under study were ground in an agate mortar to a fine powder and evenly glued on adhesive tape. Crystalline fine powder of  $\text{V}_2\text{O}_5$  was used as a reference. Experiments were carried out in the transmission mode. The intensities of incident and transmitted beams were measured using ionization chambers. The monochromator was set to the 4-crystal mode ensuring the 0.5 eV resolution of beam energy at vanadium K-edge. The XANES data, collected in the 5400–5700 eV range were normalized to unity at the high energy part of the absorption curves.

### 3. Results and discussion

X-ray absorption spectra near vanadium K-edge edge for studied glasses and for crystalline  $\text{V}_2\text{O}_5$  are shown in Fig. 1.

The XANES spectra of all glasses under study consist of an absorption edge preceded by a strong pre-edge

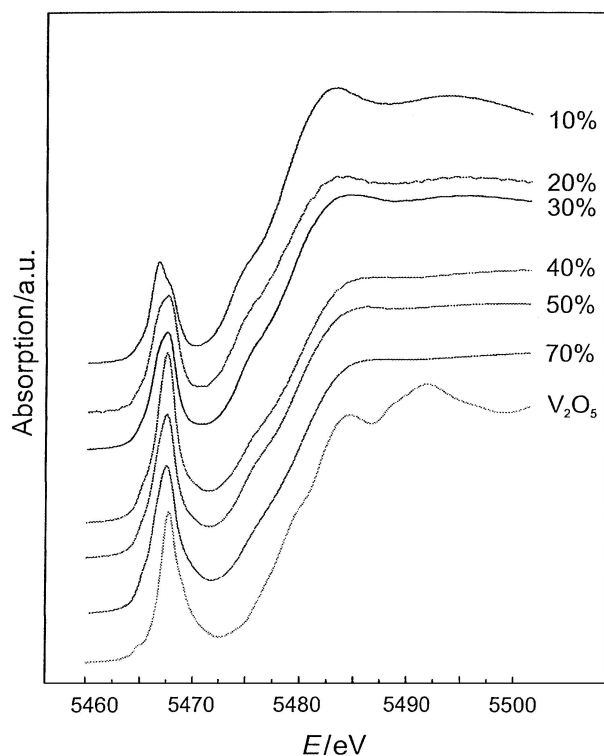


Figure 1 XANES curves at vanadium K-edge for  $\text{Li}_2\text{O}-\text{V}_2\text{O}_5-\text{P}_2\text{O}_5$  glasses of different compositions and  $\text{V}_2\text{O}_5$  crystalline powder as a reference.

peak. The absorption edge is due to  $1s-4p$  transitions of vanadium atoms. The pre-edge peak originates mainly from dipole  $1s-3d$  transitions with some contribution of quadrupole transitions. The presence of this peak gives information on the symmetry of the local vanadium environment. Since  $1s-3d$  dipole transitions are strictly forbidden for a site with the inversion symmetry, such a peak would be weak or absent if the coordination polyhedron of absorbing vanadium atoms had inversion symmetry. When the symmetry of the local environment vanadium atom is lowered,  $1s-3d$  dipole transitions become allowed due to hybridization of  $3d$  states of vanadium and  $2p$  states of oxygen [9]. Since electronic quadrupole transitions are much weaker than electronic dipole transitions, the intensity of the pre-edge feature depends on the site symmetry of vanadium atom. The lowest intensity is expected for a local symmetry with an inversion center (e.g. for octahedral coordination) when  $3d-2p$  mixing is forbidden. In contrast, for tetrahedral coordination it can have intensity comparable with an edge jump [9]. For a given geometry of the coordination polyhedron the intensity of the pre-edge absorption depends on the size of the molecular cage defined by the vanadium nearest neighbor ligands [12].

From the absorption spectra shown in Fig. 1, one can see that the positions of both pre-edge peak and the absorption edge exhibit a systematic shift to higher photon energy values upon increasing content of  $\text{V}_2\text{O}_5$  in the glasses. The shifts of the pre-edge peak positions and the modification of its shape are more pronounced in Fig. 2a. These changes are due to the evolution of relative occupancy of  $\text{V}^{4+}$  and  $\text{V}^{5+}$  valence states upon increasing  $\text{V}_2\text{O}_5$  and decreasing  $\text{Li}_2\text{O}$  contents in the glasses of the series under study.

In order to further emphasize the individual contributions of each of the two valence states a set of second derivatives of the pre-peak absorption are plotted vs. photon energy (Fig. 2b). In the case of glasses with  $\text{V}_2\text{O}_5$  content below 30%, the individual  $\text{V}^{4+}$  and  $\text{V}^{5+}$  contributions are separated to the extent enabling qualitative estimation of relative occupancy of the two charge states of vanadium. The maximum of the pre-edge feature for  $\text{V}^{4+}$  state is at 5466.6 eV. The position of the peak maximum for the  $\text{V}^{5+}$  state (5467.6 eV) for the glasses under study is the same as for the crystalline  $\text{V}_2\text{O}_5$  reference sample.

We have undertaken attempts to use non-linear fitting procedures to deconvolute the experimental pre-edge absorption peaks into two Gaussian profiles, due to  $\text{V}^{4+}$  and  $\text{V}^{5+}$  charge states respectively. The result of the fit is shown in Fig. 3. The best-fit values provide an estimate of a relative contribution of  $\text{V}^{4+}$  and  $\text{V}^{5+}$  ions. In the case of the 10% glass about 80% of vanadium atoms are in  $\text{V}^{4+}$  charge state (Fig. 3). For higher concentrations of  $\text{V}_2\text{O}_5$ , contribution of the  $\text{V}^{5+}$  state increases. However, its quantitative determination is unreliable, because of the ambiguity of the deconvolution procedure for these compositions. Energy positions of absorption edges (Fig. 1) reflect that tendency,

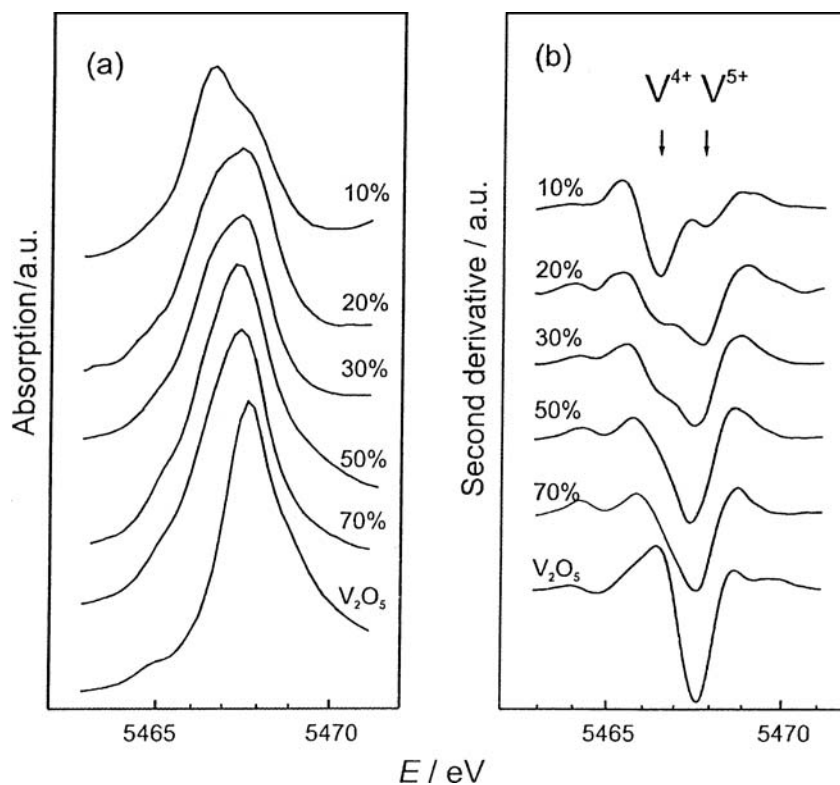


Figure 2 (a) Pre-edge peak of XANES curves for glasses of different compositions and  $V_2O_5$  polycrystalline powder, (b) second derivative of XANES pre-peak for glasses under study and  $V_2O_5$  reference sample.

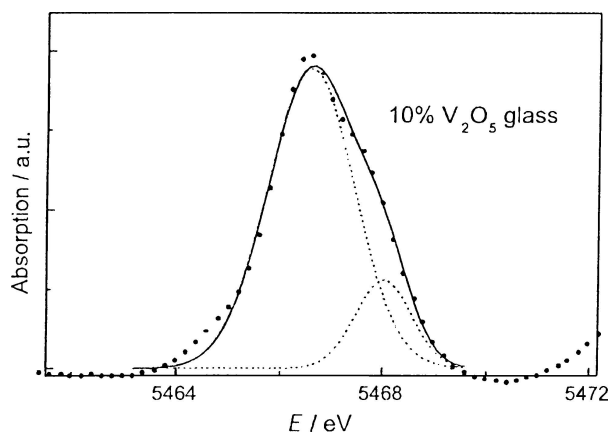


Figure 3 Deconvolution of a XANES pre-edge peak for a glass of composition  $45Li_2O \cdot 10V_2O_5 \cdot 45P_2O_5$  using two Gaussian profiles (dotted lines).

though no discernible differences in positions of the edges for the glasses with 50 and 70% of  $V_2O_5$  can be seen.

The fact that at high concentration of  $V_2O_5$  (and consequently  $V^{5+}$ ) there is still a substantial contribution of  $V^{4+}$  centers is consistent with our electronic conductivity measurements. Results of those measurements [1, 3] show that glasses of high concentration of  $V_2O_5$  (70%) exhibit substantial electronic conduction, which directly depends on the electron hopping between  $V^{4+}$  and  $V^{5+}$  centers.

#### 4. Conclusions

From XANES experiments on  $Li_2O-V_2O_5-P_2O_5$  glasses it was found that vanadium exists in two

charge states ( $V^{4+}$  and  $V^{5+}$ ). The relative contents of vanadium in each of the valence state were estimated from the deconvolution of pre-edge peak. It has been found for glasses containing a small amount of  $V_2O_5$  (e.g.  $45Li_2O \cdot 10V_2O_5 \cdot 45P_2O_5$ ) that the majority of vanadium ions are in the  $V^{4+}$  valence state. As the total content of  $V_2O_5$  increases, the relative content of vanadium ions in  $V^{5+}$  charge state also increases.

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