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Evaluation of transference numbers in mixed conductive lithium vanadate-phosphate glasses

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A method for evaluating the transference numbers in mixed electronic-ionic glasses of the Li_2O –V_2O_5–P_2O_5 system is proposed and tested, basing on the analysis of temperature dependences of the total conductivity of these glasses. The method consists of representing experimental non-Arrhenius temperature dependences of the total conductivity by a sum of two Arrhenius-like contributions. The latter ones were tentatively attributed to the electronic and ionic partial conductivities.

Key words: *mixed electronic-ionic conduction; conductive glasses; impedance spectroscopy; transference number*

1. Introduction

Lithium vanadate-phosphate glasses of the Li_2O–V_2O_5–P_2O_5 ternary system exhibit mixed electronic-ionic conduction [1, 2], which, depending on the proportions of the constituents, can be purely ionic (low V_2O_5 content), almost purely electronic (high amounts of V_2O_5) or intermediate electronic-ionic [3]. The relative ratio between the electronic and ionic components of the conduction can be controlled in a continuous way by appropriate changes in the glass composition. Ionic conduction in these glasses occurs via the motion of Li^+ ions, while electronic transport takes place by electron (polaron) hopping between aliovalent V^{4+} and V^{5+} centres present in vanadate glasses. The possibility of controlling the character of conductivity within the same system by adjusting chemical composition can be of interest for potential applications of these conductors as basic components in integrated microbatteries, solid electrolytes (ionic conducting glasses), or mixed electronic-ionic cathode materials.

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A closer look at the changes in slopes of the temperature dependences of the conductivity of lithium vanadate glasses, especially those with higher contents of V_2O_5, suggests that the character of the conductivity may depend not only on composition, but also on temperature, even at moderate temperatures [4]. In this work, we present the temperature dependences of the conductivity of mixed conductive glasses of the Li_2O–V_2O_5–P_2O_5 system and tentative analyses of these dependences in terms of temperature-dependent ionic and electronic transference numbers.

2. Experimental

The glasses were prepared by a standard melt-quenching method [4]. Reagent grade $LiNO_3$ (Aldrich), V_2O_5 (ABCR), and $NH_4H_2PO_4$ (POCh) were used in glass syntheses. A series of glasses was prepared, whose compositions are described by the formula: xLi$_2$O·(100 – 2x)V$_2$O$_5$·xP$_2$O$_5$, where x = 15, 25, 35, 40 and 45. Their compositions were additionally labelled as: A (x = 15), B (x = 25), C (x = 35), D (x = 40), and E (x = 45). The compositions of all these glasses corresponded to different values of the parameter $r = [Li_2O]/([V_2O_5] + [P_2O_5])$ which is a good measure of the extent of disruption of the glass network (formed by vanadate and phosphate polyhedra) by the glass modifier (Li_2O).

XRD measurements have confirmed the amorphous state of the as-prepared samples. Characteristic temperatures (glass transition and crystallization temperatures T_g and T_c) were determined from DSC traces taken on a Perkin-Elmer Pyris 1 apparatus, with the heating rate 20 K/min. The total electrical conductivity of the samples was determined by ac impedance spectroscopy (IS), i.e. by applying a small ac voltage and recording the current response [5]. The measurements were done in a wide temperature range (20–360 °C) using a Solartron 1260 analyzer and a temperature regulation and stabilization system [4]. Gold electrodes were sputtered onto polished opposite sides of the glasses. The electrodes were blocking for ions and reversible for electrons. The spectra were measured in the 100 mHz–10 MHz range, and the amplitude of the ac signal was set to 30 mV rms in two-electrode mode. All impedance spectroscopy measurements were fully automated and run under computer control, temperature programming included. The acquired spectra were numerically analyzed by the equivalent circuit approach [5] using the computer package [6].

3. Results and discussion

Figure 1 presents the dependence of the glass transition temperature T_g on the parameter r. It is seen that T_g values change with the composition in a step-like manner: glasses A and B with higher contents of V_2O_5 have lower values of T_g (260–280 °C), while other compositions (C, D, E) with lower amounts of V_2O_5 are characterized by a considerably higher T_g (360–370 °C). The step-like dependence of

T_g versus r indicates that there is a distinct difference in the structures of those two groups of glasses.

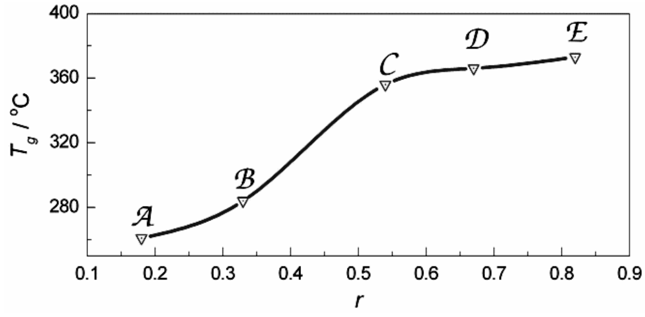


Fig. 1. Dependence of the glass transition temperature on the parameter r.
Solid line is a guide for the eye

Also, the character of the impedance spectra (not shown here – for more details and plots see Refs. [3, 4]) of the glasses under study depend on their chemical composition. The spectra of samples with a predominant electronic component consisted of a single semicircle, and predominantly ionic conducting glasses contained an additional spur at low frequencies. For intermediate cases (comparable ionic and electronic components), spectra consisted of two strongly overlapping semicircles. We also noticed that for glasses A and B the spectra change their character with temperature, from a single semicircle at room temperature to two overlapping arcs at higher temperatures.

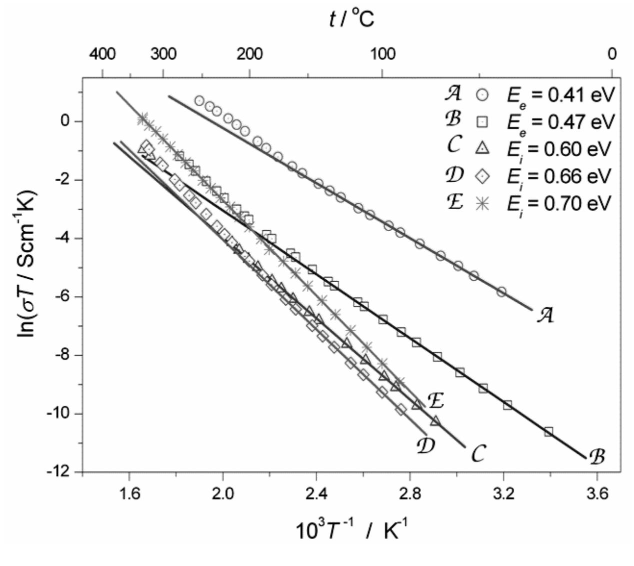


Fig. 2. Temperature dependences of conductivity for mixed conductive glasses of the composition xLi$_2$O·(100 – 2x)V$_2$O$_5$ – xP$_2$O$_5$. Glass labels: A (x = 15), B (x = 25), C (x = 35), D (x = 40), E (x = 45)

The temperature dependence of the total conductivity of the mixed conducting lithium vanadate glasses (Fig. 2) exhibit a discernible deviation from linearity at temperatures T_s well below the glass transition temperature determined from DSC. The temperature range, in which the change of slope occurs, depends on the chemical composition of the glass.

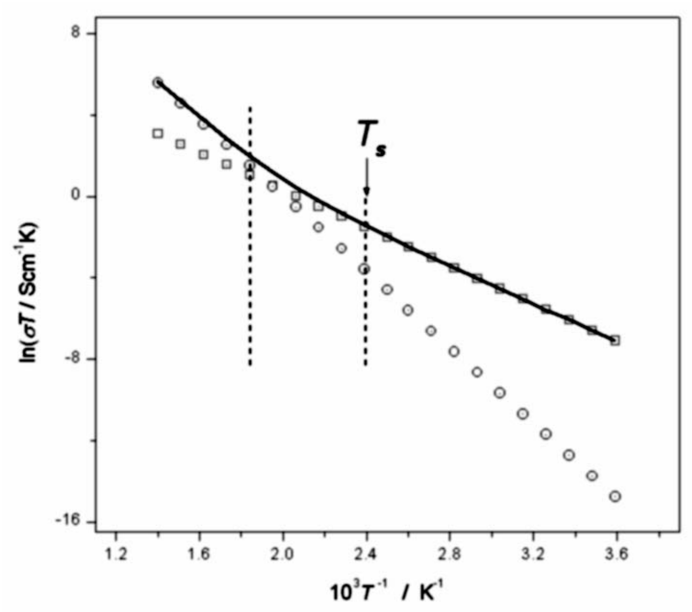


Fig. 3. Simulation of the effective conductivity of a mixed conductive glass based on the approach shortly explained in the text

In order to account for this feature, we have represented each of the experimental non-Arrhenius dependences shown in Fig. 2 by a sum of two Arrhenius-like ones with different activation energies. A model temperature dependence of that kind is shown in Fig. 3. To represent the experimental non-Arrhenius dependence by a sum of two Arrhenius-like ones, we used a standard least square fitting procedure that varies parameters of the Arrhenius formula (the preexponential factor σ_0 and activation energy E) to reach the best fit. An example of the results of such fits (for glass A; $x = 15$) is shown in Fig. 4.

We have attributed the observed effect (i.e. a gradual increase of the activation energy with temperature) to contributions of both electronic and ionic components to the total electrical conductivity. Due to different activation energies for electronic and ionic transport, the proportions between both components vary with temperature, resulting in a non-Arrhenius temperature dependence of the total conductivity.

It has been established for years that in the temperature range 20–300 °C the conductivity in electronically conducting vanadate-based solids follows the Arrhenius formula with a single activation energy E_e in the range 0.3–0.5 eV (e.g., [7]). On the other hand, the ionic conductivity in purely ionically conducting lithium glasses also depends on temperature according to the Arrhenius formula. The activation energies E_i determined in this work are in the range 0.66–1 eV. They are close to $E_i = 0.6$ eV for the ionically conducting glass $40Li_2O{\cdot}20B_2O_3{\cdot}40P_2O_5$ [8] (similar to $E_i = 0.66$ eV found in this work for the glass $40Li_2O{\cdot}20V_2O_5{\cdot}40P_2O_5$) and $E_i = 0.74$ eV for another ionically conducting glass, $50Li_2O{\cdot}50B_2O_3$ [9].

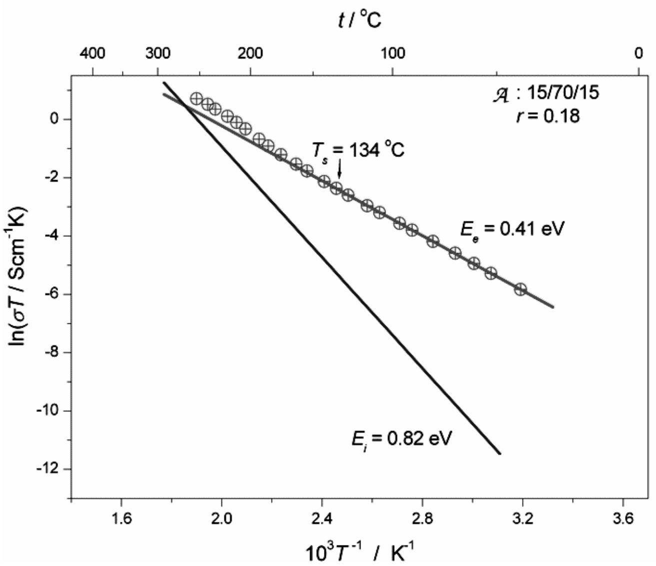
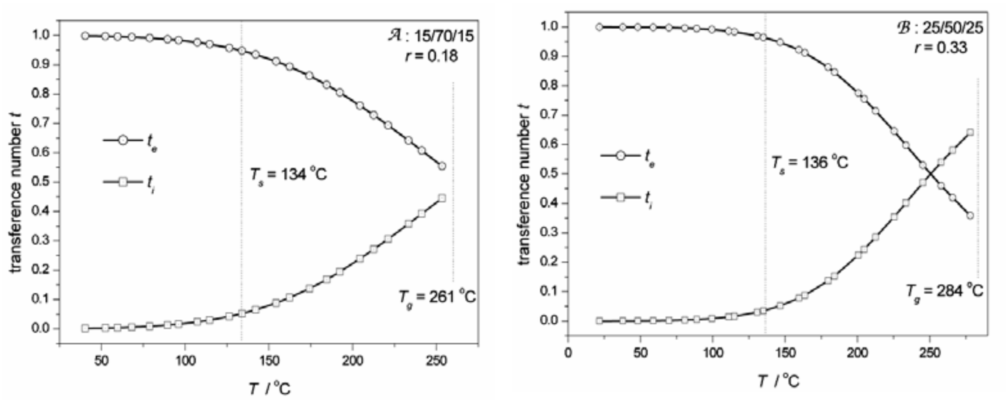


Fig. 4. Temperature dependences of the conductivities of glass A of the composition $15Li_2O{\cdot}70V_2O_5{\cdot}15P_2O_5$ (circles). The lines represent the calculated Arrhenius dependences for the electronic and ionic components of the total electrical conductivity

Since both components, electronic and ionic, are non-negligible in the glasses under study, it is natural to attribute the Arrhenius-like dependences used to reconstruct the experimental temperature dependences of conductivity to electronic and ionic components separately. We have assumed that both components are totally independent of each other.

Using the results of the aforementioned fitting procedure for the studied glasses, we determined the temperature dependences of the electronic and ionic conductivities, (σ_e and σ_i, respectively) for all glasses. Consequently, we were able to evaluate the transference numbers, electronic $t_e = \sigma_e/(\sigma_e + \sigma_i)$ and ionic $t_i = 1 - t_e$. The evaluated temperature dependences of the electronic and ionic transference numbers for glasses A, B, and D are shown in Fig. 5. Up to temperature T_s (the temperature where a change in activation starts, Figs. 2–4), one of the transference numbers (t_e for glasses A and B and t_i for glass D) is higher than 0.95 and the other is less than 0.05. Above this temperature, the difference between both transference numbers gradually decreases and they approach each other at temperatures close to T_g. Glass E, with 40

% Li_2O and only 10 % V_2O_5, exhibits a single activation energy in the whole temperature range. Due to a small content of V_2O_5, the predominance of V^{4+} centres [10], and strong disruption of the glass network, electron hopping is unlikely and the total conductivity is due to ionic transport alone ($t_i \approx 1$ and $t_e \approx 0$).



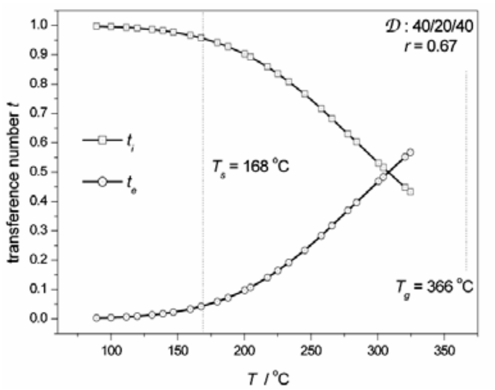


Fig. 5. Temperature dependences of the electronic and ionic transference numbers for glasses A (x = 15), B (x = 25), and D (x = 40)

Further studies on transference numbers in lithium vanadate-phosphate glasses using independent methods are planned.

4. Conclusion

A method for estimating electronic and ionic transference numbers in mixed electronic-ionic conductors from the temperature dependences of their total conductivity was proposed and applied to mixed conducting glasses of the Li_2O –V_2O_5–P_2O_5 system.

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