

Mobility of lithium ions in phosphate glass from the P_2O_5 – Li_2O – TiO_2 – SiO_2 system

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Dc and ac methods were used to calculate a diffusion coefficient and mobility of lithium ions in lithium phosphate glass of high ionic conductivity. The diffusion coefficient measured by the ac method at room temperature amounted to 2.38×10^{-12} cm²/s, as compared to 4.36×10^{-13} cm²/s obtained by the dc method. Lithium ion mobility calculated from the ac and dc methods are 9.2×10^{-11} and 1.6×10^{-11} cm²/Vs, respectively. Lithium mobility was also determined from the tracer experiment and the direct measurement of lithium penetration depth by secondary ion mass spectrometry (SIMS). SIMS results give, however, much higher value of lithium mobility (3.3×10^{-8} cm²/Vs).

Keywords: diffusion, conductivity, SIMS, lithium, phosphate glasses.

1. Introduction

Glasses with high ionic conductivity have been recently intensively investigated as a potential electrolyte material in solid state batteries [1]–[3] and for other applications, like electrochromic devices or chemical sensors [4], [5]. Lithium bearing phosphate glasses yield the highest lithium conductivity among oxide glasses [6], [7]. Transport properties of lithium in glasses has been investigated by various techniques. Since diffusion obeys Arrhenius relation, the lithium self-diffusion coefficient can be estimated from the Nernst–Einstein relation based on dc or ac impedance, measured as a function of temperature [8]–[11]. Diffusion coefficient of lithium ions is an important parameter, especially in case of materials with high ionic conductivity. Lithium ion mobility can also be calculated from the Nernst–Einstein relation or can be obtained from the direct measurement of lithium ion penetration depth. The most accurate techniques are based on the direct measurement of lithium distribution in material. It can be done using the tracer method with lithium isotope Li^6 used as a tracer [12]. Since this isotope is stable, the only method to establish its concentration is mass spectrometry. To find out the lithium concentration as a function of depth, sectioning technique is usually applied [12], [13]. Recently, the method based on dynamic

secondary ion mass spectrometry (SIMS) has been widely used in diffusion studies [14], [15]. SIMS method is more convenient because it overcomes some difficulties connected with sample sectioning and in some cases is more accurate. However, this method can only be used in case of highly homogenous samples. High error is observed in case of polycrystalline samples, especially those containing different crystalline phases due to different sputtering rates of various phases. Glasses are homogenous with some inhomogeneity regions observed on the atomic scale, so SIMS seems to be an appropriate technique in diffusion studies. The main goal of this work was to estimate the diffusion coefficient of lithium ions from dc and ac measurements and lithium ion mobility using SIMS method.

2. Experimental procedure

Glass of chemical composition $6.2\text{SiO}_2\text{--}13.7\text{P}_2\text{O}_5\text{--}4.7\text{TiO}_2\text{--Li}_2\text{O}$ was obtained by the conventional high temperature melting procedure. The batch was prepared from chemical pure reagents: Li_2CO_3 , SiO_2 , $\text{NH}_4\text{H}_2\text{PO}_4$, and TiO_2 . An appropriate mixture of reagents was first calcinated at $800\text{ }^\circ\text{C}$ during 2 hours and next melted in a platinum crucible. The melting temperature was $1250\text{ }^\circ\text{C}$. This temperature was maintained during 2 hours. The crucible was covered to avoid volatilisation losses. The melt was poured out on a stainless-steel plate and a 3 mm thick disk was formed. Next, the glass plate was placed in an electric furnace for annealing. The annealing temperature was $10\text{ }^\circ\text{C}$ bellow temperature T_g which was established on the basis of DTA measurement. The samples were prepared in the form of squares 20×20 and 2 mm thick by cutting, grinding and polishing of initial glass disks. The electrodes were prepared with colloidal graphite – (Ted Pella Inc). Electrical connections were made by spring loaded platinum electrodes. The Dc conductivity and impedance were measured at constant temperatures in the range from 40 Hz to 5 MHz using HIOKI 3532 LCR meter. Lithium isotope Li^6 in the form of LiOH from Euroisotope was used as a tracer source. The depth of lithium migration was established on the basis of SIMS depth profile measurements. VSW SIMS equipped with high-resolution FEI liquid gallium ion gun and Balzers quadrupole mass spectrometer was used for SIMS analyses. The energy of gallium ions was of 25 keV and the measurement area was $73\times 73\text{ }\mu\text{m}$ in all the cases.

3. Results and discussion

3.1. Lithium diffusion coefficient calculated with dc measurements

Lithium diffusion coefficient can be calculated from dc measurements using the Nernst–Einstein relation

$$D_{\text{dc}} = \frac{\sigma k T}{n q^2} H_R \quad (1)$$

where D_{dc} is the diffusion coefficient value obtained from the dc ionic conductivity measurements, σ – the dc conductivity, k – the Boltzmann constant, T – the

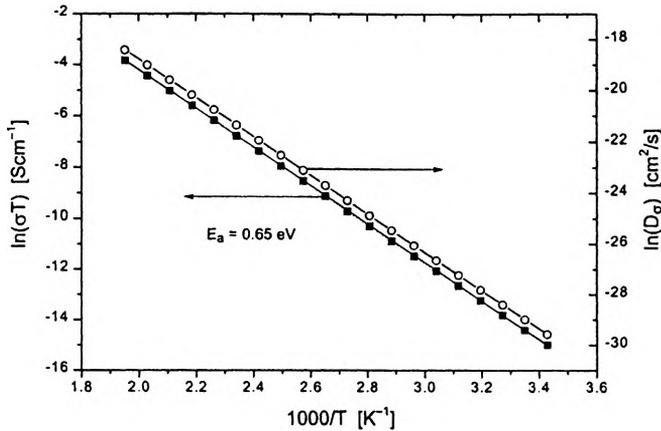


Fig. 1. Conductivity σ and diffusion coefficient D_{σ} calculated from dc measurement.

temperature, n – the number of mobile species (lithium ions in this case), q – the electric charge, and H_R – the haven ratio. It is generally observed that the haven ratio is of order of unity if one assumes that all ions are mobile, what is true in this case [16]–[18]. The number of lithium ions was calculated from chemical composition of the glass and its density equal to 2.66 g/cm^3 and was found to be $n = 1.16 \times 10^{21} \text{ at/cm}^3$. The diffusion coefficient calculated from the Nernst–Einstein relation, as a function of temperature, is shown in Fig. 1. The direct measurement of dc conductivity (based on the Ohm relation) is always done with a uncertainty due to polarisation effect, so the diffusion coefficient calculated from direct dc measurements has usually lower value than that obtained by, for instance, the ac method. This effect can be reduced if one applies voltage for a short period of time. In this study the lithium diffusion coefficient at room temperature and the activation energy of diffusion calculated from the dc measurements were $4.36 \times 10^{-13} \text{ cm}^2/\text{s}$ and 0.66 eV , respectively. Conductivity has the same activation energy (Fig. 1). This is the evidence that the conduction and diffusion mechanism have the same nature. Moreover, there is no electronic or hole conductivity in the studied system.

3.2. Ac measurement

A value of conductivity free of error due to polarisation of the sample can be achieved from ac measurements. Figure 2 shows a typical impedance plot $\text{Re}(Z) = f(-\text{Im}(Z))$ obtained at $25 \text{ }^\circ\text{C}$. The dc conductivity can be read out directly from the Nyquist diagram by extrapolating the low frequency part of the semicircle to the intercept with the real axis (Fig. 2). The dc conductivity estimated from a complex impedance plot was used to calculate the diffusion coefficient from the Nernst–Einstein relation (1). The values of the diffusion coefficient vs. temperature, based on ac measurements, is shown in Fig. 3. The value of D_{ac} at 300 K was found to be $2.38 \times 10^{-12} \text{ cm}^2/\text{s}$ and is almost one order of magnitude higher than that calculated from the dc method ($4.36 \times 10^{-13} \text{ cm}^2/\text{s}$). The lithium diffusion coefficient measured by the ac technique in

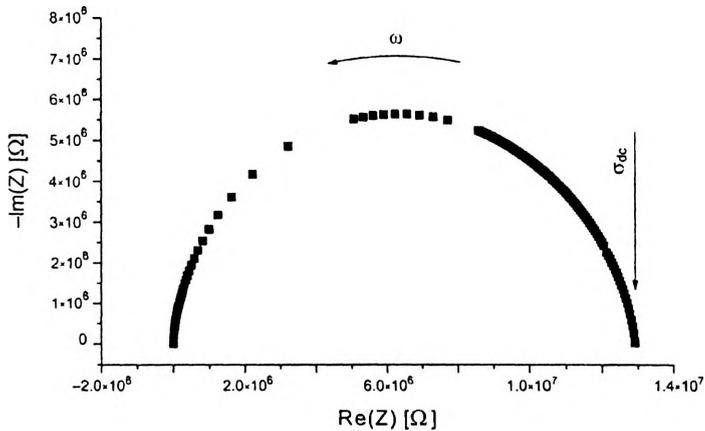


Fig. 2. Example of the Nyquist plot for lithium phosphate glass at 20 °C

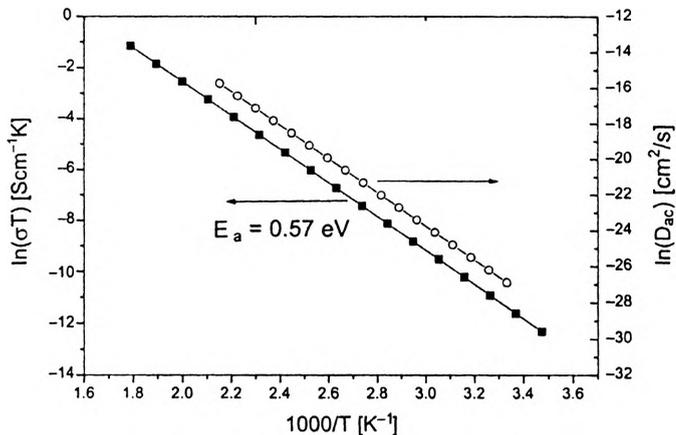


Fig. 3. Conductivity and diffusion coefficient calculated from ac measurements.

glasses from the $\text{Li}_2\text{O}-\text{V}_2\text{O}_5-\text{P}_2\text{O}_5$ system was reported to be 9.1×10^{-15} at 25 °C [19]. The activation energy of conductivity measured by the ac method is $E_a = 0.57$ eV (Fig. 3). Lower value of the activation energy of the conductivity in the case of the ac method is usually observed, and is connected with lower well potential in a glass structure under ac perturbation.

3.3. Tracer experiments

Trace diffusion experiment was carried out to estimate lithium ion mobility in the studied glass. In brief, such an experiment relies on the measurement of isotope concentration as a function of distance. Thin layers of the sample are ground away from the sample successively and the isotope concentration is being determined from mass spectrometry measurements or by radioisotope technique in case of radioactive

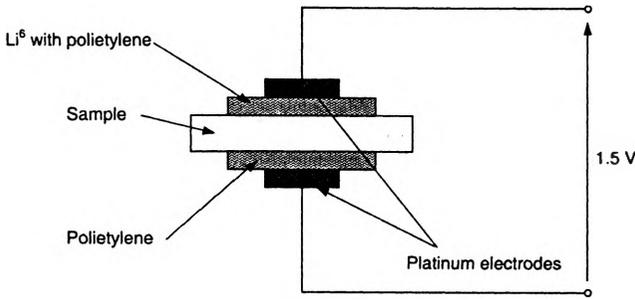


Fig. 4. Schematic drawing of isotope diffusion experiments.

isotope [12], [13]. The main difficulty lies in removing the layers, what can be done precisely only by using a special grinding machine. This problem can be avoided when SIMS depth profiling method is employed [14], [15].

In this experiment, lithium isotope was introduced into the glass sample under electric field with strength of 6 V/cm. The lithium isotope in the form of lithium hydroxide was mixed with water and polyethylene oxide and applied on the surface in the form of gel. Concentration of Li^6 ions in the gel was 10 wt%, similar to Li^7 concentration in the glass. The arrangement of the experiment is shown schematically in Fig. 4.

The time of lithium migration was measured and the migration depth was determined from SIMS measurements. Depth profile for one selected sputtering time is shown in Fig. 5. Since the natural lithium isotope Li^7 contains about 10% of Li^6 isotope, so the concentration line of Li^6 in the SIMS profile cannot be expected to go to “zero” level. The depth of SIMS crater, after 300 sputtering cycles, was measured using an optical microscope and the sputtering rate was established, allowing to estimate the lithium migration depth. Figure 6 shows the relationship between the time

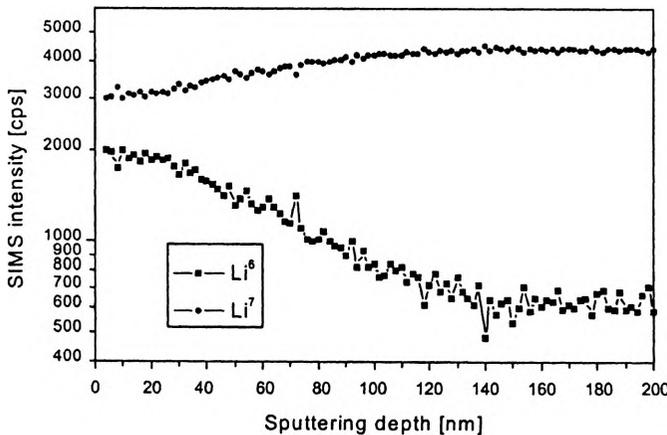


Fig. 5. SIMS depth profile. Li^6 was diffused into the glass during 225 s.

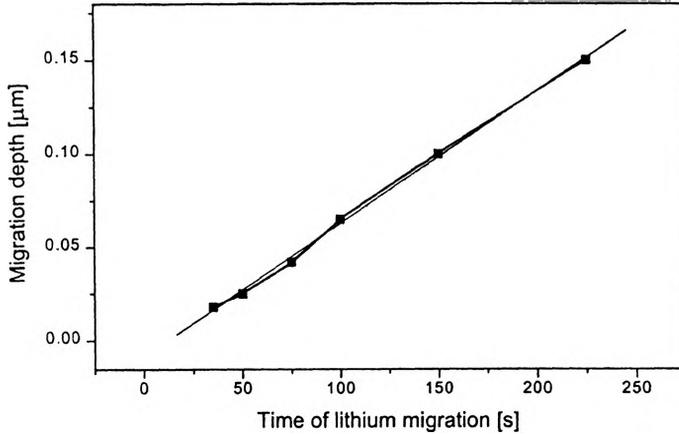


Fig. 6. Lithium ion migration depth as a function of the migration time estimated from the SIMS measurements.

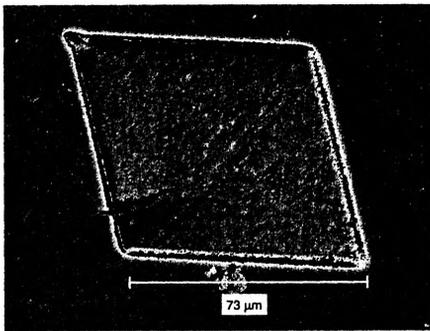


Fig. 7. SEM picture of the glass surface after the SIMS measurement.

of lithium migration and the migration depth. SIMS crater is shown in Fig. 7. The surface is smooth and uniform, which fulfils the condition of homogeneity of the sample. Mobility of lithium ions was calculated from equation

$$\mu = -\frac{v}{\text{grad } V} \quad (2)$$

where μ – the ion mobility, v – the ion velocity (taken from Fig. 6) and V – the electric potential. Lithium mobility calculated from the above relationship amounts to $\mu = 3.5 \times 10^{-7} \text{ cm}^2/\text{Vs}$. Ion mobility can also be calculated from diffusion or conductivity data:

$$\mu = \frac{\sigma_{\text{dc}}}{nq}, \quad (3)$$

$$\mu = \frac{Dq}{kT}. \quad (4)$$

Lithium ion mobility at 300 K, calculated from the above equations, gives value 9.2×10^{-11} and 1.6×10^{-11} cm^2/Vs for the ac and dc methods, respectively. Mobility estimated from the conductivity methods gives very similar results, while the SIMS dynamic method gives a much higher value. The explanation of observed differences is connected with SIMS sputtering process. Under the bombardment with the high energy gallium ions (25 keV) the lithium ions are driven into the glass matrix, so the measured depth of lithium migration is much higher. The second reason lies in the nature of the experiment. Lithium ions have been driven into the glass under high electric field (6 V/cm), while the conductivity measurements are usually carried out under low voltage (150 mV, in this study). Mobility calculated from the conductivity data is due to thermally stimulated migration of lithium in the glass, while the SIMS data give the value of the total mobility (thermal and stimulated by applied electric field).

4. Conclusions

A diffusion coefficient of lithium ions in glass from the $\text{P}_2\text{O}_5\text{-Li}_2\text{O-TiO}_2\text{-SiO}_2$ system has been measured by the dc method and impedance technique. The dc method gives a lower value of the diffusion coefficient, mainly due to polarisation effect. Mobility calculated from the dc and ac method gives similar value 1.6×10^{-11} and 9.2×10^{-11} cm^2/Vs , respectively. Dynamic SIMS technique was used to estimate mobility of the lithium ion under electric field with a strength 6 V/cm. Measured total mobility is 3.5×10^{-7} cm^2/Vs .

References

- [1] TULLER H.L., BUTTON D.P., UHLMANN D.R., *J. Non-Cryst. Solids* **40** (1980), 93.
- [2] OTTO K., *Phys. Chem. Glasses* **7** (1986), 55.
- [3] BUTTON D.B., TANDON R.P., TULLER H.L., UHLMANN D.R., *J. Non-Cryst. Solids* **42** (1980), 297.
- [4] CHOPRA N., MANSINGH A., CHADHA G.K., *J. Non-Cryst. Solids* **126** (1990), 194.
- [5] LEVY M., DUCLOT M.J., ROUSSEAU F., *J. Power Sources* **26** (1989), 381.
- [6] MALUGANI J.P., ROBERT G., *Mater. Res. Bull.* **14** (1979), 1075.
- [7] MERCIER R., MALUGANI J.P., FAHYS B., ROBERT G., *Solid State Ionics* **5** (1981), 663.
- [8] MACDONALD D.D., *Transient Techniques in Electrochemistry*, Plenum Press, New York 1977, p. 229.
- [9] SMITH D.E., [In] *Electroanalytical Chemistry*, [Ed.] A.J. Bard, Marcel Dekker, New York 1966, Vol. 1, pp. 1–155.
- [10] HUGGINS R.A., [In] *Fast Ion Transport in Solids. Electrodes and Electrolytes*, [Eds.] P. Vashishta, J. N. Mundy, G.K. Shenoy, Proc. Intern. Conf. North-Holland, Amsterdam 1979, p. 53.
- [11] BOUKAMP B.A., RAISTRICK I.D., HUGGINS R.A., [In] *Fast Ion Transport in Solids. Electrodes and Electrolytes*, [Eds.] P. Vashishta, J. N. Mundy, G.K. Shenoy, Proc. Intern. Conf. North-Holland, Amsterdam 1979, p. 177.
- [12] YONGJUAN D., FRISCHAT G.H., BEIER W., *J. Non-Cryst. Solids* **112** (1989), 399.
- [13] SCHOO U., CRAMER C., MEHRER H., *Solid State Ionics* **138** (2000), 105.
- [14] CARLSON D.E., MAGEE C.W., *Appl. Phys. Lett.* **33** (1978), 81.
- [15] GILGER S., NEBEL C.E., BAUER G.H., MOHRING H.D., *J. Non-Cryst. Solids* **77–78** (1985), 503.

- [16] KELLY J.E., III, CORDARO J.F., TOMOZAWA M., *J. Non-Cryst. Solids* **41** (1980), 47.
- [17] THOMAS M.P., PETERSON N.L., *Solid State Ionics* **14** (1984), 297.
- [18] KAHNT H., *J. Non-Crystal. Solids* **203** (1996), 225.
- [19] RADHAKRISHNAN K., CHOWDARI B.V.R., *Solid State Ionics* **51** (1992), 197.

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