Increased electrical conductivity of LiPON glasses produced by ammonolysis

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Abstract

Oxynitride phosphate glasses have been obtained by ammonolysis of xLi$_2$O $(1-x)$P$_2$O$_5$ ($x=0.5$, 0.55, 0.575) glasses and their electrical conductivity and lithium structural environment studied. Nitrided glasses were prepared through thermal treatment of the phosphate glasses under ammonia flow at temperatures below 800 °C. Nitrogen incorporation produces a sharp increase in conductivity for low nitrogen contents, while the activation energy decreases. Conductivity increase is very small or negligible for N/P ratios higher than 0.1, and the effect of nitrogen is analogous for all Li/P ratios. The increase in the electrical conductivity is explained through the structural modifications produced after the nitrogen substitution within the glass network. ^{6}Li NMR experiments show that the coordination number of Li$^+$ decreases with N/P, which is interpreted as an increase in the Li–O bonds covalence. This effect of nitrogen on the lithium environment together with the increased glass density is thought to be counteracting the increase of conductivity for high nitrogen contents.
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1. Introduction

The development of new solid inorganic electrolytes for application in all solid-state lithium secondary batteries is currently one of the key issues in this technology [1,2]. The most important requirements of the electrolyte materials in battery applications are a high ionic conductivity with negligible electronic contribution and compatibility with the electrode materials. Unlike liquid electrolytes, the use of solid electrolytes in rechargeable batteries may provide numerous advantages such as high reliability, thermal and mechanical stability, no self-discharge and longer active life, absence of contamination of the electrode materials minimizing the risk of explosion, as well as the possibility of miniaturization through thin-film production.

The synthesis of LiPON thin-film electrolytes by sputtering of crystalline Li$_3$PO$_4$ targets in N$_2$ atmosphere and its successful application in lithium microbatteries [3] was the starting point of many studies on LiPON solid electrolytes as well as other related compounds, e.g. LiSiPON [4,5]. LiPON electrolytes show a conductivity of 2×10^{-6} S cm^{-1} at room temperature and activation energy of 0.55 eV [3]. Furthermore, they may also work as protective layers for metallic lithium anodes [6], so that lithium metal can be used as the anode material in lithium batteries and thus allowing higher energy and power densities than when graphitized anodes are used as intercalation anode materials. The amorphous character of the material and the presence of nitrogen increase the conductivity with respect to that of the crystalline compound. The observed increase in conductivity is supposed to be related to the formation of P–N bonds, which replace P–O ones, leading to a more reticulated anionic network.

The first studies on alkali oxynitride phosphate glasses by Marchand [7] constituted the basis for the research on LiPON electrolytes due to their improved properties when nitrogen substitutes oxygen. After nitridation, the chemical durability, as well as the mechanical and thermal stability of the phosphate

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glasses, drastically increases. Moreover, in lithium oxynitride phosphate glasses the electrical conductivity has been found to increase [8].

Nevertheless, only a few studies are known on the electrical conductivity of oxynitride phosphate glasses [8–10]. In contrast, the thermal and chemical properties as well as the structure of oxynitride phosphate glasses have been largely characterised [11–14]. During the nitrogen/oxygen substitution, both bridging (BO) and non-bridging oxygens (NBO) are substituted by dicoordinated $-N=(N_d)$ and tricoordinated $-N<(N_t)$ nitrogen species [13]. The oxynitride glass network is then formed by PO_4 and the new PO_3N and PO_2N_2 tetrahedra [13], which increase the cross-linking density giving rise to a notable modification in the glass properties. The nitridation process is carried out through well established substitution rules defined by the equivalences $2N_t=3BO$ and $2N_d=2NBO+1BO$, which are based on the substitution of $3O^{2-}$ by $2N^{3-}$, as proposed by Marchand et al. [15]. O_{1s} XPS characterisation of oxynitride phosphate glasses, as reported by Le Sauze [16] and Muñoz et al. [14], showed the variation in the relative proportions of bridging and non-bridging oxygens as a function of nitrogen content. The results indicated that the BO/NBO ratio fits the calculated values when using the nitridation model of Marchand et al. [15], showing a decrease in the relative percentage of BO and an increase in the percentage of NBO, within the range of N/P studied.

The aim of the present work is to study the role of composition and structural changes on the electrical conductivity of lithium phosphorus oxynitride glasses. Three series of lithium phosphate glasses with increasing lithium and nitrogen contents have been synthesized by thermal treatment under ammonia flow and their electrical conductivity studied as a function of the nitrogen content. The lithium environment has also been studied by ^6Li Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) and its role on the ionic conductivity is discussed as a function of the increasing nitrogen content.

2. Experimental

2.1. Synthesis of oxynitride glasses

Lithium phosphate glasses with composition $x\mathrm{Li_2O}\cdot(1-x)$ $\mathrm{P_2O_5}$ ($x=50, 55, 57.5$ mol%), have been obtained by conventional melt-quenching technique. Stoichiometric amounts of reagent grade raw materials Li_2CO_3 (Aldrich, 99%) and $(NH_4)_2HPO_4$ (Merck, 99%) were weighed and mixed. The batches were calcined in porcelain crucibles held in an electric furnace up to 450 °C, and then melted in a gas furnace (propane/air) during 1 h at temperatures ranging from 800 °C to 1000 °C depending on composition. During the melting of the glasses, the oxygen content in the furnace atmosphere was measured with a Thermox flue gas analyzer from AMETEK and it was determined to be between 6 and 10% O_2. The compositions of the three base glasses are given by their molecular formula as $LiPO_3$, $Li_{1.22}PO_{3.11}$ and $Li_{1.35}PO_{3.18}$ for Li_2O contents of 50, 55 and 57.5 mol%, respectively.

Oxynitride lithium phosphate glasses were obtained through ammonolysis of the base glasses in an Al_2O_3 gas-tight tube furnace at temperatures from 600 °C to 750 °C and treatment times of 3 h.

Base glasses are placed in graphite moulds acting as individual "crucibles" of 2 cm in diameter and 5 mm deep. A rectangular graphite plate with up to 8 hollow spaces containing the base glass samples was used. The furnace was heated up to the treatment temperature at a constant heating rate of 10 K min^{-1} under N_2 flow. The nitrogen flow was then switched to NH_3 (<400 ppm H_2O) during the treatment time and switched back to nitrogen while the furnace was allowed to freely cool down. Nitrided glass samples presented a light greyish colour due to graphite surface contamination but appear transparent and bubbles free.

2.2. Characterisation of the glasses

Nitrogen contents in oxynitride glasses were determined in a differential N_2/O_2 LECO TC-436 analyzer. At least three analyses were performed for each sample maintaining the experimental conditions. The N/P ratio is expressed by the x value in the molecular formula of the three series of oxynitride glasses prepared: $LiPO_{3-3x/2}N_x$ (base glass $LiPO_3$), $Li_{1.22}PO_{3.11-3x/2}N_x$ (base glass $Li_{1.22}PO_{3.11}$) and $Li_{1.35}PO_{3.18-3x/2}N_x$ (base glass $Li_{1.35}PO_{3.18}$). The average standard deviation in the nitrogen determination is ±0.3 wt.%, i.e. ±0.02 in the N/P ratio.

Glass transition temperature has been determined by Differential Thermal Analysis (DTA) in a Netzsch STA-409 analyser using a platinum crucible in air and at a constant heating rate of 10 K min^{-1}. Glass density has been measured by the Archimedes method in water at room temperature.

Electrical conductivity measurements were performed by Electrochemical Impedance Spectroscopy (EIS) in a Solartron SI1260 impedance analyzer, in the frequency range from 10 Hz to 10 MHz at temperatures between 40 and 200 °C. The samples were cut into discs of 1–2 mm in thickness and ∼10 mm in diameter and gold electrodes were sputtered on both faces as contacts for electrical measurements. The electrical conductivity (σ) is determined, for each temperature, through the resistance value (R) read at the low frequency intersection of the semicircle with the x-axis in the Nyquist plots and the sample geometric factor (e/A; e=thickness, A=electrode area) following $\sigma=e/(R\cdot A)$. The error in the conductivity determination is estimated to be 10%.

^6Li MAS NMR spectra were recorded on a BRUKER 800 MHz (18.8 T) spectrometer at a frequency of 117.748 MHz and a spinning rate of 20 kHz. The pulse length was 2.0 μs ($\pi/2$) and a 5 s recycling time was used. The recycling time used was verified to be sufficient to enable relaxation. The chemical shift reference was a 1 M LiCl solution. ^6Li nucleus is less sensitive than ^7Li (0.2 and 3.7 vs. ^{13}C, respectively), but its broader chemical shift range gives better structural information. Nevertheless, the lower sensitivity is compensated by the use of a high-field spectrometer (18.8 T).

3. Results

3.1. Characterisation of oxynitride glasses

Fig. 1 depicts the Nyquist diagrams of the base glass $LiPO_3$ determined at 95, 125 and 148 °C (a) and of its respective nitride glass $LiPO_{2.57}N_{0.29}$ determined at 94, 122 and 146 °C (b).
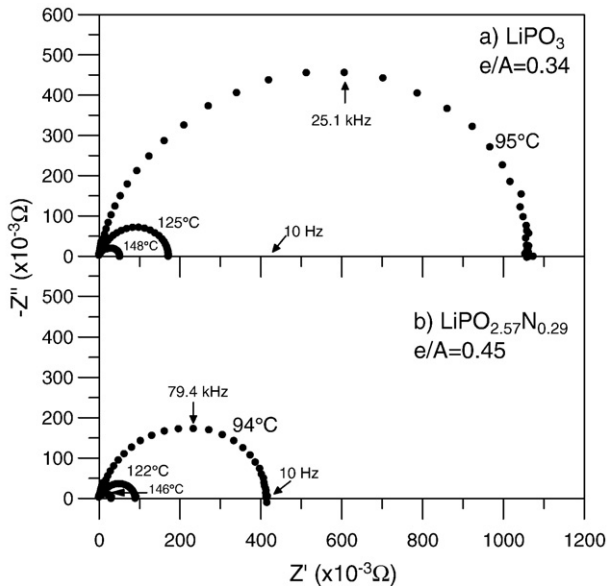
Fig. 1. Nyquist diagrams of the base glass $LiPO_3$ for 95, 125 and 148 °C (a) and of its respective nitride glass $LiPO_{2.57}N_{0.29}$ for 94, 122 and 146 °C (b).

Table 1 gathers the activation energy for conductivity and the Log(σ_0) for the three series of oxynitride phosphate glasses, their corresponding analysed nitrogen contents in wt.% N_2, glass transition temperatures and densities. A sharp decrease in the activation energy takes place for the lowest nitrogen content in the three series of glasses, while the E_a remains quite similar for further nitrogen incorporation. The pre-exponential factor also tends to decrease with increasing nitrogen content. As already observed in previously studied oxynitride phosphate glasses, nitrogen incorporation produces an increase in both T_g and glass density, which is related to the increase in the cross-linking density of the glass network due to the more covalent P–N and P=N bonds.

Fig. 2 shows the logarithm of electrical conductivity at 25 °C and the activation energy for the three base glasses as a function of the Li/P ratio in the glass composition. Values on Fig. 2 are in
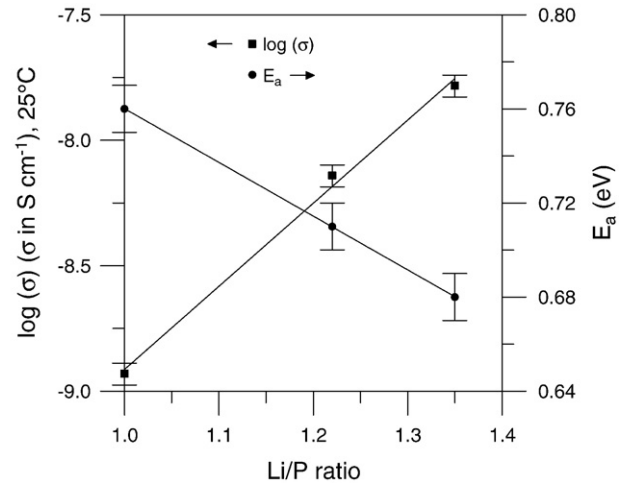

Fig. 2. Conductivity extrapolated at 298 K and activation energy as a function of the Li/P ratio for the base glasses $LiPO_3$, $Li_{1.22}PO_{3.11}$ and $Li_{1.35}PO_{3.18}$. Lines represent the least-square fits of the data points.

accordance to previously published data [8,17,18]. A linear relationship is observed for both the activation energy and the room temperature conductivity.

Fig. 3 depicts the logarithm of electrical conductivity as a function of the reciprocal absolute temperature for the $LiPO_3$ base glass and corresponding oxynitride glasses with Li/P = 1 ($LiPO_{3-3x/2}N_x$). The experimental data follow, within the temperature range studied, an Arrhenius law:

$$\sigma = \sigma_0 \exp(-E_a/kT) \qquad (1)$$

where σ_0 and k are the pre-exponential factor and the Boltzmann constant, respectively, and E_a is the activation energy for conduction. The Arrhenius plots of the other two series of oxynitride glasses (Li/P = 1.22, 1.35) are similar and thus omitted. At first sight, an increase in the electrical conductivity as well as an
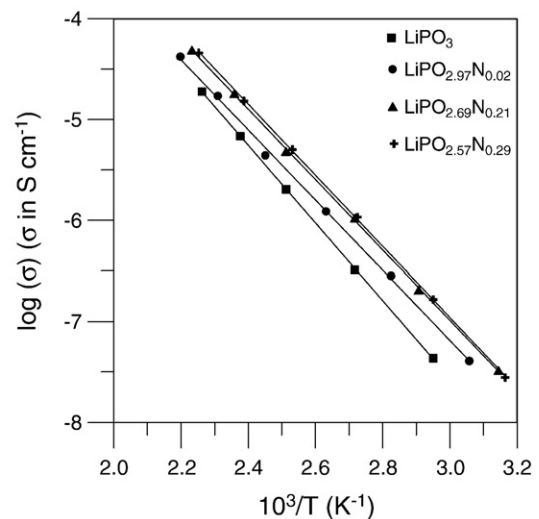
Table 1
Nitrogen contents in wt.% N_2, glass transition temperature, density, activation energy for conductivity (E_a) and pre-exponential factor (Log(σ_0)) for the base and oxynitride phosphate glasses

Glass	wt.% N_2	T_g	density (g cm^{-3})	E_a (eV)	Log(σ_0)
	(±0.3)	(±2 °C)	(±0.01)	(±0.01)	(σ_0 in S cm^{-1})
$LiPO_3$	–	311	2.33	0.76	4
$LiPO_{2.97}N_{0.02}$	0.4	329	2.32	0.69	3.2
$LiPO_{2.69}N_{0.21}$	3.6	n.m. [a]	2.38	0.69	3.5
$LiPO_{2.57}N_{0.29}$	5.0	n.m. [a]	2.39	0.70	3.6
$Li_{1.22}PO_{3.11}$	–	310	2.35	0.71	3.9
$Li_{1.22}PO_{3.03}N_{0.05}$	0.8	318	2.38	0.62	2.9
$Li_{1.22}PO_{2.93}N_{0.12}$	1.9	334	2.37	0.66	3.4
$Li_{1.22}PO_{2.80}N_{0.21}$	3.5	351	2.40	0.64	3.3
$Li_{1.35}PO_{3.18}$	–	309	2.36	0.68	3.7
$Li_{1.35}PO_{2.99}N_{0.13}$	2.1	327	2.38	0.60	2.9
$Li_{1.35}PO_{2.73}N_{0.30}$	4.7	343	2.42	0.63	3.3

[a] Not measured.

Fig. 3. Arrhenius plots for conductivity of the glass series $LiPO_{3-3x/2}N_x$ (x = 0.02, 0.21 and 0.29).
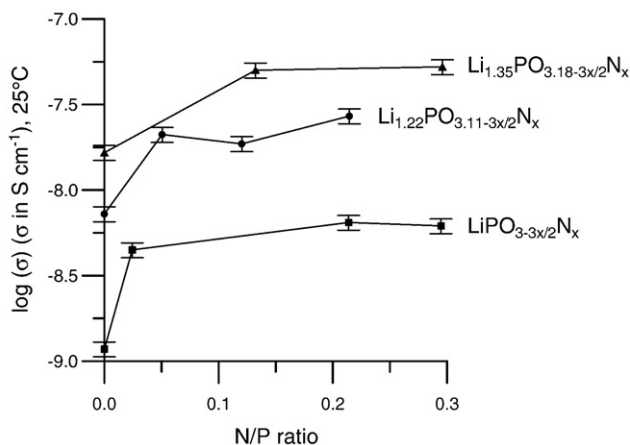
Fig. 4. Variation of the logarithm of conductivity extrapolated at 298 K as a function of the N/P ratio in the oxynitride phosphate glasses of the series $LiPO_{3-3x/2}N_x$, $Li_{1.22}PO_{3.11-3x/2}N_x$ and $Li_{1.35}PO_{3.18-3x/2}N_x$. The lines are drawn as a guide to the eyes.

appreciable change in the Arrhenius slopes can be observed for the oxynitride compositions as compared to the base glasses.

Fig. 4 depicts the $Log(\sigma)$ at 25 °C, extrapolated from the Arrhenius fits, as a function of the N/P ratio for all three investigated series of oxynitride glasses, $LiPO_{3-3x/2}N_x$, $Li_{1.22}PO_{3.11-3x/2}N_x$ and $Li_{1.35}PO_{3.18-3x/2}N_x$. A sharp increase in $Log(\sigma)$ is observed from low nitrogen contents up to N/P ~ 0.1, with a further asymptotic increase in $Log(\sigma)$ to a maximum depending on the composition. The highest conductivity found was 5.3×10^{-8} S cm^{-1} for the glass $Li_{1.35}PO_{2.73}N_{0.30}$, and the maximum difference in σ between the base glasses and the maximum N/P ratio is more than half order of magnitude in the three series. The sharp increase in σ for the lowest nitrogen contents indicates that the influence of E_a on conductivity prevails over that of σ_0. These data also evidence that once a small amount of nitrogen is incorporated into the glass network, the maximum conductivity and the minimum activation energy are reached for each Li/P ratio.

3.2. Lithium environment studied by NMR

Fig. 5 shows the ^{6}Li MAS NMR spectra for two of the series of oxynitride phosphate glasses, $LiPO_{3-3x/2}N_x$ (a) and $Li_{1.35}PO_{3.18-3x/2}N_x$ (b). One broad resonance, characteristic of a distribution of local environments typical of amorphous systems, is found in the spectra of the base glasses $LiPO_3$ and $Li_{1.35}PO_{3.18}$ at chemical shifts of -0.90 ppm and -0.79 ppm, respectively. The observed ^{6}Li chemical shifts are comparable to those found in glasses of the binary system xLi_2O $(1-x)$ P_2O_5 $(5 < x < 55$ mol%) studied by Alam et al. [19]. In their work, the authors determined a linear increase in the ^{6}Li chemical shift as the Li_2O content increases along with a coordination number (CN) for the Li^+ in the range of 4 to 5 for the studied compositions. Alam et al. [19] interpret that the increase in the chemical shift of ^{6}Li is due to the decrease in the average coordination number of lithium ions.

The observed increase in the chemical shift of the ^{6}Li NMR resonances with nitrogen has been related to a decrease in the

average Li^+ coordination number and to an increase in the covalent character of Li–O bonds [19]. Such an effect of nitridation on the cationic environment has already been observed in $Li_{0.25}Na_{0.25}Pb_{0.25}PO_{3-3x/2}N_x$ glasses, where ^{207}Pb NMR spectra showed an increase in the chemical shift of the ^{207}Pb NMR resonance band [13]. The CN of the Pb^{2+} ions decreases with nitrogen content and the covalency of the Pb–O bonds increases, i.e. PbO *former character* increases.

For the three oxynitride glass series studied in this work, a shift of the resonance bands to higher ^{6}Li chemical shifts is also observed when the nitrogen content increases, i.e. from -0.90 ppm ($LiPO_3$) to -0.79 ppm ($LiPO_{2.57}N_{0.29}$) and from -0.79 ppm ($Li_{1.35}PO_{3.18}$) to -0.64 ppm ($Li_{1.35}PO_{2.73}N_{0.30}$). Thus, the effect of increasing Li_2O or introducing nitrogen into

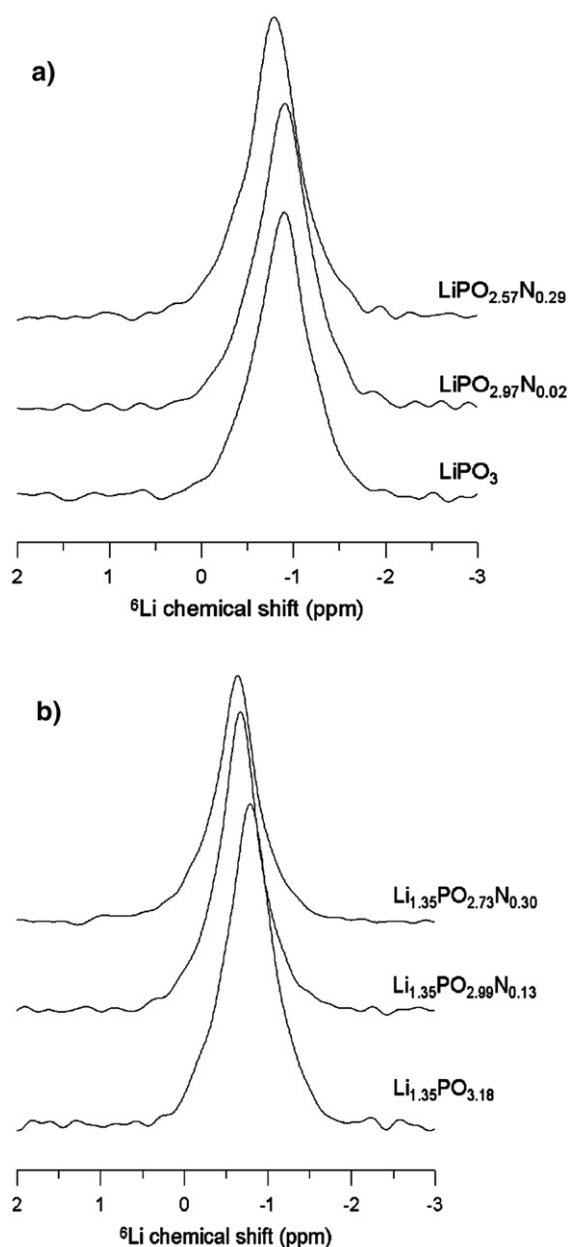Fig. 5. ^{6}Li MAS NMR spectra of oxynitride glasses $LiPO_{3-3x/2}N_x$ (a) and $Li_{1.35}PO_{3.18-3x/2}N_x$ (b).

the glass network produces the same modification of the chemical shift due to the decrease of the CN(Li$^+$). This confirms that the incorporation of nitrogen into the glass network clearly affects the lithium environment.

4. Discussion

In the present study, the conductivity sharply increases up to N/P ~ 0.1 for all the Li/P ratios studied (1, 1.22 and 1.35), while maintaining very similar values for higher N/P (Fig. 4). Wang et al. [8] reported an increase in the electrical conductivity of some oxynitride lithium phosphate glasses after nitrogen incorporation, which was also more pronounced for very low N/P ratios. The authors concluded that for glasses with high lithium and nitrogen contents a lower increase might be due to the presence of bubbles in the samples [8]. However, a possible influence of bubbles on the conductivity behaviour is excluded from the results obtained here because the glasses were all transparent, homogeneous and bubbles free. This indicates that nitrogen affects the electrical conductivity according to the structural modifications of the glass network induced by nitridation.

The reason for the increase in the electrical conductivity in phosphate as well as in silicate oxynitride glasses remains not completely explained. Unuma *et al.* [20,21] and Wang et al. [8] assumed that the increased cross-linking density of the glass network after nitridation has the same role on conductivity as the mixed anion effect. By using the model of Anderson and Stuart [22], Wang et al. [8] proposed that the decrease in the electrostatic energy when P–O bonds are replaced by the more covalent P–N ones may cause the increase in the ionic conductivity through the decrease in the electrostatic activation energy [22]. However, Unuma and co-workers *et al.* [20,21] also pointed out that an increase in the network-strain energy by incorporation of nitrogen should produce the opposite effect, i.e. an increase in the total activation energy for conductivity. Thus, the effect of nitrogen incorporation into the glass network still remains controversial.

As observed in all previous oxynitride phosphate systems, T_g and density data (see Table 1) suggest that the network connectivity increases with increasing nitrogen content. Since 3 oxygen atoms are substituted by only 2 nitrogen atoms, and nitrogen is lighter than oxygen, the increase in density clearly indicates that the structure of the oxynitride glasses is more compact than that corresponding to the oxide base glass. The increased cross-linking density, by formation of the P–N and P=N bonds, produces new and stronger connections among the phosphate chains. At the same time, the proportion of non-bridging oxygens is increasing with respect to the total amount of both BO and NBO, as introduced above. Thus, we suggest the following mechanism to explain the effect of nitrogen on the conductivity behaviour: at the beginning of nitridation, a higher cross-linking density introduced by nitrogen atoms should facilitate the lithium transfer between phosphate chains; in the same way, the higher amount of NBO generated by nitridation could increase the number of hopping positions for Li$^+$ ions, creating conduction paths with lower activation energy with the consequent rising of the electrical conductivity.

On the other hand, both T_g and glass density, as well as the proportion of NBO, increase linearly within the range of N/P ratios studied, so it looks difficult to explain the almost constant conductivity values for N/P > 0.1.

Different effects might be counteracting the increase in electrical conductivity experienced for low N/P; the most important may be related to the lithium structural environment. Although ^{31}P NMR spectra indicate a continuous formation of P–N bonds [13,16] for increasing N/P ratio, ^{6}Li NMR spectra are particularly affected for high nitrogen contents, meaning that lithium coordination is modified only when the quantity of P–N bonds is enough for affecting the lithium coordination by local constraints. The increase in the covalent character of Li–O bonds, together with the progressive increase in the glass density at high nitrogen contents, could neutralize the increase in the conductivity, then explaining the almost constant value observed for high N/P.

Even though the room temperature conductivity of the oxynitride glasses studied in this work is still lower than the values reported for the LiPON thin-film electrolytes [3], further research is currently on progress in order to achieve oxynitride compositions with higher lithium contents and, therefore, higher ionic conductivities. At the same time, the addition of a second network former oxide, such as SiO$_2$ or B$_2$O$_3$, is expected to produce an increase in conductivity. This, combined with the nitrogen incorporation, could result in a way for producing highly conductive oxynitride glasses through the conventional glass melting method followed by the ammonolysis reaction.

5. Conclusions

The influence of the nitrogen content on the electrical conductivity of lithium phosphorus oxynitride glasses has been studied. For all Li/P ratios, the conductivity increases with increasing nitrogen while the activation energy diminishes. The effect of nitrogen incorporation is quite important for low N/P ratios and almost stabilized for N/P > 0.15.

The increase in the electrical conductivity of the oxynitride glasses for low nitrogen contents is thought to be due to the increase in the amount of non-bridging oxygens and the increased cross-linking density of the glass network, which create conduction paths with lower activation energy. For high nitrogen contents, the increase in the covalent character of Li–O bonds as seen by ^{6}Li NMR may counteract the lithium mobility giving rise to a quite constant value of electrical conductivity.

Acknowledgements

References

[1] B. Scrosati, Electrochimica Acta 45 (2000) 2461.
[2] A.G. Ritchie, J. Power Sources 136 (2004) 285.

[3] X. Yu, J.B. Bates, G.E. Jellison Jr., F.X. Hart, J. Electrochem. Soc. 144 (2) (1997) 524.

[4] S.-J. Lee, J.-H. Bae, H.-W. Lee, H.-K. Baik, S.-M. Lee, J. Power Sources 123 (2003) 61.

[5] S.-J. Lee, H.-K. Baik, S.-M. Lee, Electrochem. Comm. 5 (2003) 32.

[6] K.-I. Chung, W.-S. King, Y.-K. Choi, J. Electroanal. Chem. 566 (2004) 263.

[7] R. Marchand, C. R. Acad. Sci. Paris Ser. II 294 (1982) 91.

[8] B. Wang, B.S. Kwak, B.C. Sales, J.B. Bates, J. Non-Cryst. Solids 183 (1995) 297.

[9] L. Pascual, A. Durán, Phys. Chem. Glasses 37 (3) (1996) 92.

[10] F. Munoz, R. Keding, C. Rüssel, R. Marchand, A. Durán, L. Pascual, Phys. Chem. Glasses: Eur. J. Glass Sci. Technol. A 47 (1) (2005) 58.

[11] F. Munoz, A. Durán, L. Pascual, R. Marchand, Phys. Chem. Glasses 43C (2002) 113.

[12] F. Munoz, A. Durán, R. Marchand, L. Pascual, Phys. Chem. Glasses 44 (6) (2003) 416.

[13] F. Munoz, L. Pascual, A. Durán, L. Montagne, G. Palavit, R. Berjoan, R. Marchand, J. Non-Cryst. Solids 324 (2003) 142.

[14] F. Munoz, L. Pascual, A. Durán, R. Berjoan, R. Marchand, J. Non-Cryst. Solids 352 (2006) 3947.

[15] R. Marchand, D. Agliz, L. Boukbir, A. Quémerais, J. Non-Cryst. Solids 103 (1988) 35.

[16] A. Le Sauze, PhD Thesis, *Université de Rennes 1* (1998), Rennes (France).

[17] J.P. Malugani, G. Robert, Mat. Res. Bull. 14 (1979) 1075.

[18] M. Doreau, A. Abou El Anouar, G. Robert, J. Chim. Phys. 78 (3) (1981) 223.

[19] T.M. Alam, S. Conzone, R.K. Brow, T.J. Boyle, J. Non-Cryst. Solids 258 (1999) 140.

[20] H. Unuma, S. Sakka, S., J. Mater. Sci. Lett. 6 (1987) 996.

[21] H. Unuma, K. Komori, S. Sakka, J. Non-Cryst. Solids 95&96 (1987) 913.

[22] O.L. Anderson, D.A. Stuart, J. Ame. Ceram. Soc. 37 (12) (1954) 573.