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Effect of fluorine and nitrogen on the chemical durability of lithium phosphate glasses

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ABSTRACT

The dissolution of glasses belonging to the systems of composition $xLi_2O\cdot(100-x)P_2O_5$ ($x = 38$–55 mol%) and $(55-x/2)Li_2O\cdot xLiF\cdot(45-x/2)P_2O_5$ ($x = 10$–30 mol%), with and without nitrogen, has been studied through immersion of the samples in water at 95 °C using a Soxhlet extractor. In this work, a wide range of compositions prepared by melting has allowed a detailed study of the effect of nitrogen and fluorine in the chemical properties of glasses with variable lithium contents. In lithium phosphorus oxynitride glasses, it was demonstrated that low lithium and high nitrogen contents improve the chemical durability. However, there is a maximum of nitrogen percentage from which the durability is not further improved. In lithium phosphorus fluoro-oxynitride glasses, fluorine introduction leads to a deterioration of the phosphate glasses; however, the introduction of nitrogen in these glasses increases significantly the chemical durability. The structural changes obtained by NMR and XPS are used to explain the effect of lithium, fluorine and nitrogen on the chemical properties. In general, the decrease of non-bridging oxygens and the increase percentage of phosphorus groups with nitrogen increase the chemical resistance.

1. Introduction

Amorphous materials based on lithium phosphate are good candidates as solid electrolytes in lithium batteries [1–3]. One of the specific characteristics that solid state electrolytes must fulfill is a high chemical durability; however, lithium phosphate glasses generally present a poor chemical stability.

According to literature [4–6], the reaction between the phosphate glasses and water is produced into two steps. 1) Diffusion process: the ionic exchange between Li^+ close to non-bridging oxygens (NBO) and the protonated species, which is proportional to $t^{1/2}$. 2) Hydrolysis process: the dissolution of the phosphate chains as a consequence of the breaking of P–O–P bonds, that depends on time (t). In phosphate glasses [7–9], it has been seen that the introduction of nitrogen produces an increase of the chemical durability of several orders of magnitude, which is explained through the structural changes produced by nitridation process.

Two systems which have been studied as solid electrolytes are lithium phosphorus and fluoro-phosphorus oxynitride glasses due to the N and LiF introduction produces the increase of ionic conductivity [10–13]. In the case of chemical properties, the addition of nitrogen in phosphate glasses [14–16] produces the enhancement of the cross-linking density due to the substitution of oxygen by nitrogen, leading to the formation of P–N bonds with higher covalence than P–O bonds. On the contrary, the introduction of fluorine in phosphate glasses conducts to the depolymerization of the network by the breaking of phosphate chains, forming PO_3F or PO_2F_2 species [12,17–20]. This depolymerization could be responsible for the decrease of chemical durability in fluorophosphates glasses, but, no references have been found analyzing the effect of immersion in water of these glasses.

This work is focused on the study of the chemical durability in lithium phosphorus oxynitride and fluoro-oxynitride glasses through immersion in distilled water at 95 °C. The effect on chemical stability produced by the introduction of lithium, fluorine and nitrogen has been analyzed and is related to the evolution of the structure of phosphate glasses.

2. Experimental

2.1. Preparation of LiPON glasses

Lithium phosphate glasses in the system $xLi_2O\cdot(100-x)P_2O_5$, where $x = 38, 40, 45, 50$ and 55 mol%, and the oxynitride glasses corresponding to the base compositions with 38, 45 and 55 mol% Li_2O were prepared using melt-quenching and ammonolysis techniques previously described by Mascaraque et al. [13]. The glasses were prepared from batches of reagent grade materials: Li_2CO_3 (99% ACS Reagent, Aldrich) and $(NH_4)_2HPO_4$ (99% ACS. Reagent, Merck). The batches were calcined for 1 day in porcelain crucibles in an electric furnace up to 400 °C, then melted for 2 h at 800–850 °C, depending on the composition, and cast onto brass plates to quench the melt. To obtain the oxynitride glasses,

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the samples with 38, 45 and 55 mol% Li_2O were nitrided following a thermal treatment under flowing anhydrous ammonia at 750 °C for 2, 5 and 7 h.

2.2. Preparation of LiPOFN glasses

Lithium fluorophosphate glasses in the system $(40 - x/2)Li_2O{\cdot}xLiF{\cdot}(60 - x/2)P_2O_5$, where x = 10 and 30 in mol%, and their corresponding oxy-fluoro-nitride glasses were prepared using a two step melting process previously designed by Mascaraque et al. [12]. Firstly, the parent glass ($40Li_2O{\cdot}60P_2O_5$) was prepared as described above, then nitrided at 750 °C during 2 and 5 h and, finally, re-melted with different amounts of LiF (99%, Merck). The glass and LiF mixtures were melted in porcelain crucibles in an electrical furnace under nitrogen flow at 800 °C during 1 h and poured onto brass molds.

2.3. Characterization of the glasses

Nitrogen analyses were carried out in a nitrogen/oxygen LECO TC-436 analyzer by the inert gas fusion method. N/P is calculated through the following equation:

$$\frac{N}{P} = \frac{\frac{M_{bass\ glass}}{10} \cdot \text{wt.\% N}}{140 + \text{wt.\% N}} \quad (1)$$

being $M_{base\ glass}$ the molecular mass of the glass without nitrogen and wt.% N the nitrogen content as obtained by the LECO TC-436 analyzer. The maximum deviation in the N/P atomic ratio is ±0.02 N/P units.

Ion selective electrode technique was used to analyze fluorine. The samples were previously dissolved with 1 mL hydrochloric acid in 200 mL deionized water.

The chemical durability, measured through the resistance of the glasses to dissolution in water, has been determined following the weight loss after immersion of the sample in water at 95 °C as a function of time. Fig. 1 shows the experimental setup consisting on a Soxhlet extractor, a reflux tube, a bottom flask of 250 mL and a heating plate.

3. Results

Table 1 shows the analyzed nitrogen and nominal lithium contents in mol%, and the formula of the LiPON glasses. The nitrogen content increases with the increasing nitridation time length. Table 2 presents the nominal lithium, nominal and analyzed fluorine, and analyzed nitrogen for LiPOFN glasses. There is a fluorine loss around 80%, except for the glass 40/10FN5 with a fluorine loss of 25%. Besides, the glasses nitrided during 5 h, 40/10FN5 and 40/30FN5, have almost the same fluorine content, and so only the chemical properties of 40/10FN5 will be studied, due to the lower loss of fluorine after the second melting.

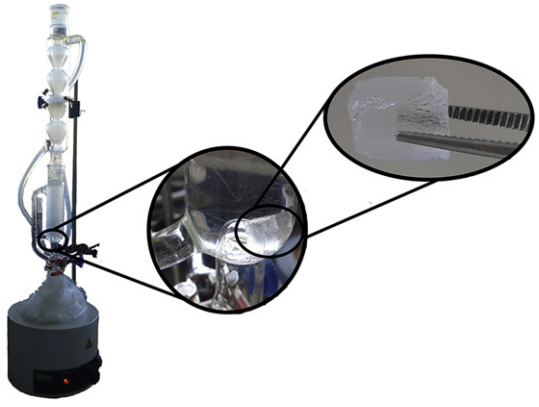

Fig. 1. Experimental setup for measuring the chemical durability.

Table 1
Mol% of nominal lithium and analyzed nitrogen of LiPON glasses.

$xLi_2O{\cdot}(100 - x)P_2O_5$ (x = 38, 45, 55 mol%)			
Glasses	$Li_{nominal}$ (mol%)	$N_{analyzed}$ (±0.3 mol%)	Formula
38/62	13.9	0.0	$Li_{0.61}PO_{2.81}$
$38/62N_2$	13.9	2.9	$Li_{0.61}PO_{2.57}N_{0.16}$
$38/62N_4$	13.9	4.4	$Li_{0.61}PO_{2.46}N_{0.24}$
$38/62N_7$	13.9	5.2	$Li_{0.61}PO_{2.40}N_{0.28}$
45/55	17.3	0.0	$Li_{0.82}PO_{2.91}$
$45/55N_2$	17.3	2.1	$Li_{0.82}PO_{2.75}N_{0.11}$
$45/55\ N_4$	17.3	4.0	$Li_{0.82}PO_{2.60}N_{0.21}$
$45/55N_7$	17.3	5.2	$Li_{0.82}PO_{2.51}N_{0.27}$
55/45	26.1	0.0	$Li_{1.22}PO_{3.11}$
$55/45N_2$	26.1	3.6	$Li_{1.22}PO_{2.85}N_{0.17}$
$55/45N_4$	26.1	4.8	$Li_{1.22}PO_{2.78}N_{0.22}$
$55/45N_7$	26.1	5.8	$Li_{1.22}PO_{2.70}N_{0.27}$

3.1. LiPON glasses

The weight loss in water has been determined for the base and oxynitride glasses. Fig. 2 plots the weight loss of the lithium phosphate base glasses as a function of time. To determine the lithium effect on the chemical durability, the dissolution rate of the base glasses was calculated as a function of the lithium content, (Fig. 3). The lower the lithium content of the base glasses the lower is the weight loss with time, several days were necessary to observe the complete dissolution; however, the sample with 55 mol% Li_2O, without nitrogen, is completely dissolved in only 12 min. It is clear that the introduction of lithium in phosphate glasses leads to the deterioration of their chemical resistance by hydrolysis. Indeed, the glass with 55 mol% Li_2O presents a dissolution rate of ca. 80 times higher than the glasses with the lowest lithium content (≤45 mol%).

Fig. 4 plots the weight loss of $Li_yPO_z - {}_{3x/2}N_x$ ($0.61 \le y \le 1.22$; $2.81 \le z \le 3.11$ and $0.16 \le x \le 0.27$) glasses as a function of time. It is observed that the increase of nitrogen in the glass network produces the decrease of weight loss for all the series. From the linear fit of the three series, the dissolution rate (D_R) could be obtained as a function of N/P ratio, as represented in Fig. 5. The nitrogen introduction leads to lower dissolution rates. Thus, significantly improving the chemical durability of lithium phosphate glasses, as expected from previous studies [8,9,21,22]. The inset of Fig. 5 shows the D_R for glasses with N/P higher than 0.1, showing values of D_R much smaller than those obtained for the non-nitrided glasses.

3.2. LiPOFN glasses

Fig. 6a) and b) shows the weight loss percentage as a function of time for the fluorophosphate glasses without and with nitrogen. The introduction of fluorine produces the decrease of chemical durability for all the studied glasses. In the case of the system without nitrogen, the glasses are dissolved within 15 and 50 min (Fig. 6a). However, the nitrogen introduction improves significantly the resistance to dissolution, being 3 times the dissolution of fluorophosphate samples (Fig. 6b).

Fig. 7a) and b) depicts the dissolution rate vs the fluorine and nitrogen contents, obtained from the linear fits of Fig. 6, taking in account the range of data with linear behavior. Fig. 7a indicates that the higher the fluorine content, the higher is the dissolution rate. This increase is counteracted by the effect of nitrogen introduction, as observed in Fig. 7b, where the addition of nitrogen produces the decrease of the D_R.