LETTER TO THE EDITOR

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Letter to the Editor

Structure and electrical properties of a new thio-phosphorus oxynitride glass electrolyte

Nerea Mascaraque [a], Hiromichi Takebe [b], Gregory Tricot [c], José Luis G. Fierro [d], Alicia Durán [a], Francisco Muñoz [a,*]

[a] Instituto de Cerámica y Vidrio (CSIC), Kelsen 5, Cantoblanco, 28049 Madrid, Spain
[b] Graduate School of Science and Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan
[c] LASIR UMR CNRS 8516, Université de Lille 1, 59655 Villeneuve d'Ascq Cedex, France
[d] Instituto de Catálisis y Petroquímica (CSIC), Marie Curie 2, Cantoblanco, 28049 Madrid, Spain

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ABSTRACT

For the first time, a thio-phosphorus oxynitride glass containing nitrogen and sulfur, LiPOSN, has been prepared by a melting process in two steps and its manipulation is possible in air without any decomposition. The anionic substitution of oxygen by sulfur and nitrogen in the phosphate glass structure has been confirmed by 1D ^{31}P solid state NMR and XPS. The 2D ^{31}P DQ-SQ experiment indicates that S bearing phosphate groups are integrated into the global phosphate network and do not form clusters. Through the study of the properties of this glass, it was verified a decrease of the glass transition temperature, due to the depolymerization of the phosphate network when lithium sulfide is introduced into the oxynitride glass, along with a pronounced increase of the ionic conductivity, that suggest that this glass can be considered as a new highly conductive and corrosion resistant glass electrolyte.

Phosphate glasses used as solid state electrolytes in lithium batteries [1–3] must present a high ionic conductivity, negligible electronic conductivity, thermal and chemical stability and compatibility with the electrodes. Nowadays, Li_2S-P_2S_5-P_2O_5 glasses are the materials with the highest ionic conductivity and better performance to be used as solid electrolytes. Many authors have reported on these materials in thin films [4], powders [5] and bulk glasses [6]. Minami and Ohtomo [7,8] demonstrated that the introduction of P_2O_5 and Li_2O in the system of Li_2S-P_2S_5 produces an increase of the ionic conductivity. The sulfide-based electrolytes generally present lithium ion conductivity higher by several orders of magnitude with respect to oxide-based electrolytes. However, the main disadvantage of Li_2S-materials is their poor chemical durability, which leads to their degradation in air. One way to improve the durability may be the introduction of nitrogen [9,10] that also increases the ionic conductivity [11–13] and thermal stability [10]. So, it would be expected that phosphate glasses presenting both sulfur and nitrogen may give rise to materials with a higher ionic conductivity and a suitable chemical durability.

In this preliminary work, a new glass with composition $Li_{1.62}PO_{2.84}S_{0.11}N_{0.32}$ was prepared through a melting process in two steps developed by Mascaraque et al. [14] for obtaining LiPOFN glasses. The properties were studied by Differential Thermal Analysis (DTA) and Impedance Electrochemical Spectroscopy (EIS) in order to determine the glass transition temperature (T_g) and the ionic conductivity (σ). The structural characterization was performed by 1D ^{31}P magic angle spinning nuclear magnetic resonance (MAS-NMR), 2D ^{31}P double quantum-single quantum (DQ-SQ) MAS-NMR and X-ray photoelectron spectroscopy (XPS). The structural results confirm the anionic substitution of sulfur in the LiPON glass network as well as a substantial increase of ionic conductivity.

The process of obtaining the thio-phosphorus oxynitride glass, $Li_{1.62}PO_{2.84}S_{0.11}N_{0.32}$, started from the parent glass $55Li_2O\cdot 45P_2O_5$ [11], prepared from appropriate batch of reagent grade materials: Li_2CO_3 (99% ACS Reagent, Aldrich) and $(NH_4)_2HPO_4$ (99% ACS, Reagent, Merck), calcined for 1 day in porcelain crucibles in an electric furnace up to 400 °C, then melted for 2 h at 850 °C, and casted onto brass plates to quench the melt. The glass was nitrided following a thermal treatment under flowing anhydrous ammonia [15] at 750 °C for 5 h. The thio-phosphorus oxynitride glass was then prepared through a second melting step of the oxynitride glass ($Li_{1.22}PO_{2.60}N_{0.34}$) mixed with reagent grade material Li_2S (99%, Merck). The batch was melted in a vitreous carbon crucible covered with a silica tube under nitrogen flow at 650 °C during 30 min, as described in [16,17]. After melting, the crucible is broken to obtain the sample ($Li_{1.62}PO_{2.84}S_{0.11}N_{0.32}$).

Nitrogen and sulfur elemental analysis was carried out using a LECO CHNS-932. The errors of nitrogen and sulfur analysis are ±0.3 and ±0.2 mol%, respectively. The starting nitrogen content of sulfur-

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* Corresponding author.
E-mail address: fmunoz@icv.csic.es (F. Muñoz).

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oxynitride ($Li_{1.62}PO_{2.51}S_{0.11}N_{0.32}$) glass is maintained almost constant after the second melting; meanwhile there is a loss of sulfur of ~50% with respect to nominal sulfur added.

The two-step melting process allows combining sulfur and nitrogen into the phosphate glass, together with high lithium contents. The main advantage of this process is to obtain a sulfur-oxynitride glass that can be manipulated in air and after two years, this glass does not present any degradation.

All the ^{31}P MAS-NMR experiments were performed on a 9.4 T Bruker spectrometer at 162.9 MHz. The 1D MAS-NMR spectra was conducted at a spinning frequency of 15 kHz with a 4 mm probe-head. The experiments were recorded with a 4 μs pulse length (π/2 pulse angle), a radio-frequency (rf) strength of 60 kHz and 128 transients separated by a recycle delay (rd) of 60 s (it was checked that longer rd (120 s) does not induce any evolution of the relative proportions between the different sites). The 2D ^{31}P through space correlation map has been acquired at a spinning frequency of 30 kHz on a 2.5 mm probe-head with the DQ-SQ sequence using the BABA excitation scheme [18]. The 788×38 points have been recorded with t1-increment of 33 μs and an excitation time of 400 μs. Due to the short excitation time, the spatial proximity highlighted here can be reasonably considered as evidence for chemical connectivity. Each direct slice has been recorded with 128 transients separated by a rd of 90 s. Solid $(NH_4)H_2PO_4$ (ADP) was used as secondary reference with a chemical shift of 0.81 ppm with respect to H_3PO_4 (85%).

Photoelectron spectra (XPS) were obtained with a VG Escalab 200R spectrometer equipped with an MgKα ($h\nu = 1253.6$ eV, 1 eV $= 1.6302 \times 10^{-19}$ J) X-ray source, powered at 120 W. The XPS data signals were taken in increments of 0.07 eV with dwell times of 50 ms. Binding energies were calibrated relative to the C 1s peak at 284.8 eV. Atomic ratios were computed from experimental intensity ratios and normalized by atomic sensitivity factors [19].

The glass transition temperature, T_g, was determined by Differential Thermal Analysis (DTA) in a TG-ATD8120 (Rigaku) which employs glass lumps of around 1–2 mm, in platinum crucible, constant heating rate of 10 °C/min under argon flow and between 25 and 800 °C. T_g error is within ±5 °C.

Ionic conductivity measurements were performed in a VMP3 impedance analyzer from BioLogic, in the frequency range from 10 Hz to 1 MHz at temperatures between 25 and 70 °C. The area of the sample was 0.5×0.5 cm^2 and the thickness of 0.3 cm. The electrodes were obtained by painting both faces with silver paste (silver conductive paint, Electrotube®). The Nyquist plot of complex versus real impedance allows determining the sample resistance (R) which is read to the intersection point with the horizontal axis. The conductivity (σ) is calculated using the equation:

$$\sigma = (1/R) \cdot (l/A) \tag{3}$$

being (l/A) the sample geometric factor, where l is thickness and A is sample area.

The glass structure has been studied through 1D ^{31}P MAS NMR and 2D ^{31}P DQ-SQ MAS NMR. Fig. 1a presents the 1D spectrum of ^{31}P MAS NMR for $Li_{1.62}PO_{2.84}S_{0.11}N_{0.32}$ glass, showing three broad signals at −19, −2 and 35 ppm. The first resonance corresponds to Q^2 groups [20], following the notation by Lippmaa et al. [21] where n in Q^n groups represents the number of bridging oxygens. The second broad and asymmetric resonance could correspond to different groups as Q^1 and phosphorus species with nitrogen, PO_3N [23] and PO_2N_2 [23,24], due to the incorporated nitrogen in the glass. The third peak at 35 ppm corresponds to $(PSO_3)^{3-}$ species, as seen in thiophosphate glasses by Larink et al. [22].

The application of correlation NMR allows obtaining a more detailed analysis of the phosphate structure. Fig. 1b shows the ^{31}P DQ MAS NMR spectrum of the $Li_{1.62}PO_{2.51}S_{0.11}N_{0.32}$ glass. The 2D map, sketched with the simple quantum ^{31}P MAS NMR spectra in the direct (horizontal axis) and the double quantum spectrum in the indirect (vertical axis) dimension traces the spatial proximity (considered here as chemical connectivity) between each phosphate site. In addition to the broad and uninformative signals showing auto-correlation between the peaks around −2 ppm (B–B), the 2D spectrum clearly shows an off-diagonal signal (A–B) indicating that the $(PSO_3)^{3-}$ groups interact with the phosphorus species with or without nitrogen and participate in the global phosphate network. The lack of A–A auto-correlation also suggests the absence of $(PSO_3)^{3-}$ clustering and indicates that the P bearing S species are incorporated within the phosphate matrix.

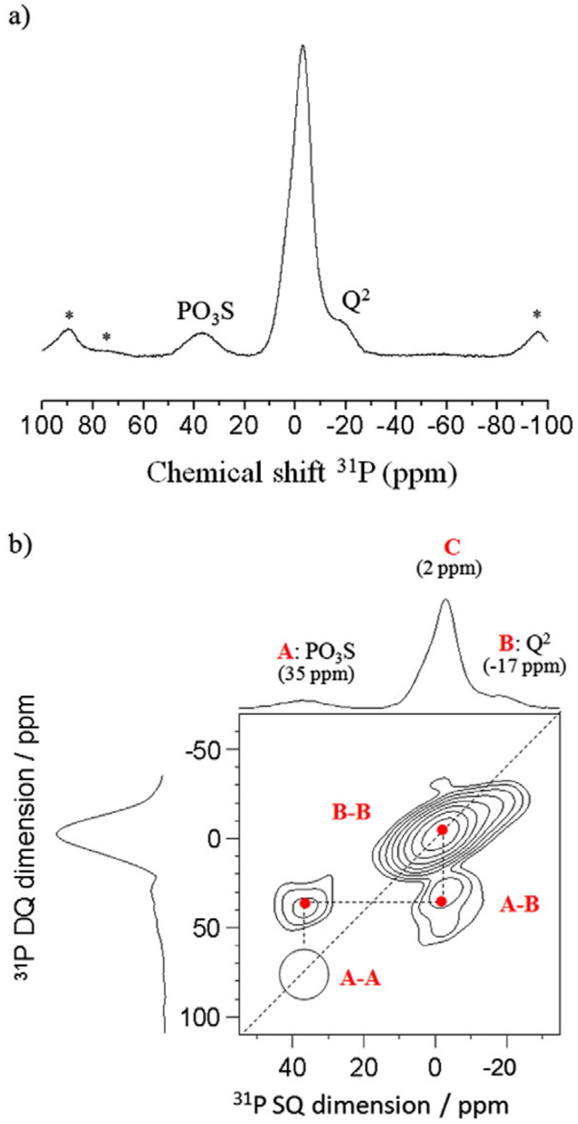

Fig. 1. 1D ^{31}P MAS NMR spectrum of the $Li_{1.62}PO_{2.84}S_{0.11}N_{0.32}$ glass performed (*ssb are spinning sidebands) a), and 2D ^{31}P DQ-SQ spectrum (minimum level corresponds to 13% of maximum intensity) b).

Through XPS, the ratios between bridging and non-bridging oxygens (BO/NBO), tri- and di-coordinated nitrogen species (N_t/N_d), and bridging and non-bridging sulfur atoms (BS/NBS) may be calculated. Fig. 2 represents the XPS spectra in the binding energy region of the N_{1s} peak a), S_{2p} b) and O_{1s} c) of the $Li_{1.62}PO_{2.84}S_{0.11}N_{0.32}$ glass. The N_{1s} spectrum of Fig. 2a was fitted to two Gaussian–Lorentzian mixed components attributed to N_t at 398.4 eV and N_d at 399.2 eV [25]. Similarly, the S_{2p} spectrum of Fig. 2b was fitted into two components, corresponding to BS at 162.9 eV and NBS at 161.7 eV [26]. Finally, the O_{1s} peak in Fig. 2c was fitted into three components assigned to NBO, P=O and $Li^+ \ldots{}^-O-P$, at 529.7 and 531.1 eV, respectively, and BO at 532.8 eV,