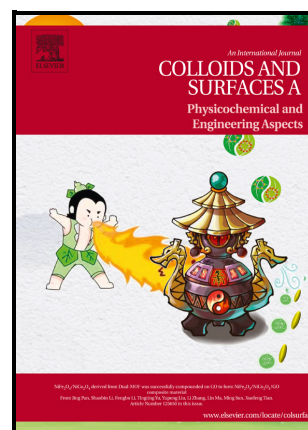


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S. TERNY, E. CARDILLO, S. BAROLIN, M.A. FRECHERO



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# Bridging oxygens, the key to the electrical behaviour improvement of an ionic liquid - glass composite.

S. Terny<sup>a</sup>, E. Cardillo<sup>b</sup>, S. Barolin<sup>c</sup> and M. A. Frechero<sup>a\*</sup>

<sup>a</sup>Dpto. de Química-Universidad Nacional del Sur- INQUISUR- CONICET, Bahía Blanca, Argentina.

<sup>b</sup>Dpto. de Química - Universidad Nacional del Sur- CIC, Bahía Blanca, Argentina.

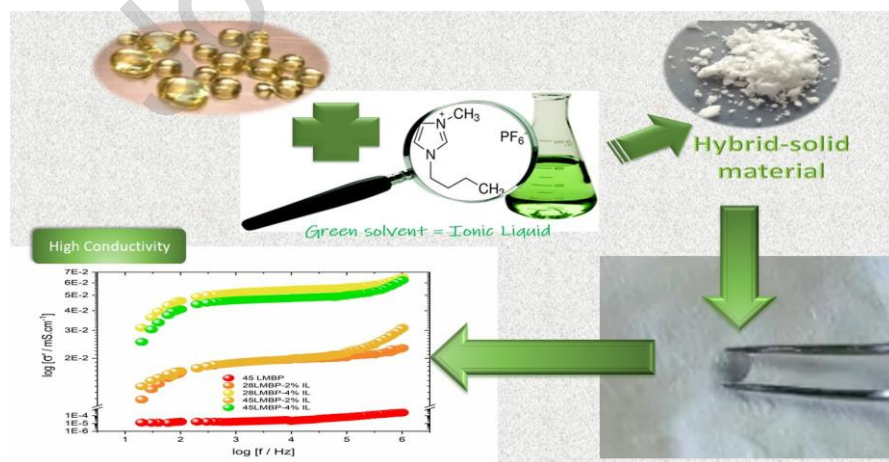
<sup>c</sup> LMC, IFIR, Universidad Nacional de Rosario, Santa Fe, Argentina.

Corresponding Author: [frechero@uns.edu.ar](mailto:frechero@uns.edu.ar) ; [mfrecher@ucm.es](mailto:mfrecher@ucm.es)

## Abstract

The interactions between the [BMIM][PF<sub>6</sub>] -ionic liquid- and a phosphate glassy surface is studied through calorimetric, structural and impedance spectroscopy methods. A soft solid conductor material is obtained mixing the ionic glass powder with the ionic liquid in a low proportion (2 and 4%). At microscopic level, the interactions of this ionic liquid with the glassy particle surfaces reveal the formation of new bridging oxygens. Therefore, the material electrical conductivity increases in more than four orders of magnitude. This finding uncovers the essential elements to be considered before incorporating an additional salt to develop a solid electrolyte.

## Graphical abstract



Keywords

IL-glass interactions; Soft conductor; Solid Electrolyte

## 1. Introduction.

Solid state batteries need a solid electrolyte with high ionic conductivity and the ability to intimately connect with electrode surfaces. Additionally, it is important to develop simple synthesis methods with low environmental impact of components and processes. Many kinds of materials have been proposed as a potential solid electrolyte where crystalline or glass ceramics are good options because they fit many of the properties sought. However, the contact between those electrolytes and electrode materials require more attention in order to reduce the internal battery resistance caused by such interphase.

Some years ago, soggy-sand materials, the combination of an inner substrate to support an ionic liquid on the surface as a medium in which the lithium ions reach a remarkably high mobility, were introduced [1]. It was proposed that they allow a high ionic ( $\text{Li}^+$ ) conductivity and a low anion migration with an appropriate wettability of the electrode that improves the mechanical stability [2].

On the other hand, it should be highlighted that ionic liquids show an extremely high thermal stability with the great advantage of an exceptionally low vapor pressure, properties that are appreciated in technical applications. However, in the field of technological applications, whether to ignore relevant mass losses by the temperature effect (evaporation or decomposition) should be carefully considered. Thus, it should be pointed out that the interactions between an ionic liquid and a metal oxide substrate affect its thermal stability. In general, ionic liquids on oxide surfaces have lower thermal stability than in bulk and, it becomes significant depending on the surface acidity metal-oxide and the Lewis basic character of the ionic liquid anion [3].

The working hypotheses behind the use of ionic liquids in this way are that such materials behave as a quasi-liquid electrolyte and that they do not leak, reaching a remarkably high ionic conductivity. However, the substrate is not always as inert as it is expected and, in the present work, we show firstly, the chemical interaction as a function of the temperature between the BMINPF6 (IL) and an ionic conductor phosphate glass as a function of its glass composition, secondly, the electrical response of this material composed by the glass plus the IL (hereafter: GIL) but without any extra salt added.

In order to understand the innermost origin of the electric charge carried when an external electric field is applied, it is important to highlight the necessity to study the interaction mechanism that takes place in the interphase between the glassy substrate (not inert) and the IL chosen previous to add an extra salt of a specific cation.

## 2. Experimental.

Samples of general formula  $x\text{Li}_2\text{O}\cdot(47.6-x)\text{MgO}\cdot(4.8\text{Bi}_2\text{O}_3\cdot47.6\text{P}_2\text{O}_5)$  (hereafter:  $x\text{LMPB}$  with  $28 \leq x \leq 45$ ) were prepared by conventional melt quenching technique using reagent grade chemicals:  $\text{MgCO}_3$ ,  $\text{Li}_2\text{CO}_3$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{H}_2(\text{NH}_4)\text{PO}_4$  [4]. The formula proportion of each component were weighed properly to obtain 10 g of each sample. The powders were well mixed in an agate mortar and next, they were placed in a platinum crucible. After the decarboxylation and ammonia elimination process the mix was heated at 1123 K for two hours in an electric furnace with regular atmosphere. During the heating process the crucible was shaken to homogenize and to remove gases in the melt. Next, the molten material was poured on a preheated aluminium plate and held for annealing at 150°C for 2 hours. Each glass sample was powdered in an agate mortar and, mixed thoroughly with the ionic liquid (IL) for 20 minutes. The ionic liquid chosen was 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF6] (Sigma- Aldrich CAS 174501-64-5; MM: 284,18  $\text{g}\cdot\text{mol}^{-1}$ ;  $\delta= 1.38 \text{ g}\cdot\text{cm}^{-3}$ ); two different ratios were studied: 2% and 4% w/w (to add the IL, a micropipette was used). The obtained material (glass + IL: GILs) is a soft

powder as figure 1 shows. Therefore, such powder was pressed in 10 mm diameter pellets during 10 minutes with 5 metric tons (the total IL content was kept below 5% / w/w to avoid leakage from pellets).

Malvern Nano ZS90 was used for measuring the electrophoretic mobility of glassy particles at 25.0°C which was automatically determined through the Smoluchowski equation in a suspension of 0.1 g L<sup>-1</sup> (milli-Q water) equilibrated by sonication.

The sample amorphous nature was tested with a Philips X Pert Pro in continuous scan mode (Cu-45KV- 30mA, 2θ range: 10°-60°, T<sub>ROOM</sub>).

The thermal stability of the pristine glasses and GILs was studied by Thermogravimetric Analysis (DTG-60H, Shimadzu). Also, a Differential Scanning Calorimetry Q20- 0836 was employed to record the heating rate a 10 K min<sup>-1</sup> of 15–20 mg of powdered sample to find the glass transition temperature (T<sub>g</sub>). Each T<sub>g</sub> value was obtained from the middle point of the C<sub>p</sub> jump during the heating (±1°C TQA software).

Density measurements of necked glasses were performed by the Archimede's principle in an analytical scale using 2-propyl alcohol as a standard secondary liquid, at room temperature.

Impedance measurements were carried out with an Agilent LCR meter 4284A (20Hz - 1·10<sup>6</sup> Hz; AC voltage of 10mV) in a temperature range between room temperature and 15°C bellow the glass's T<sub>g</sub>. Samples were prepared in disk-shaped pellets as describe above and each face pellet was coated uniformly with a thin layer of silver paint to have proper electrical contact.

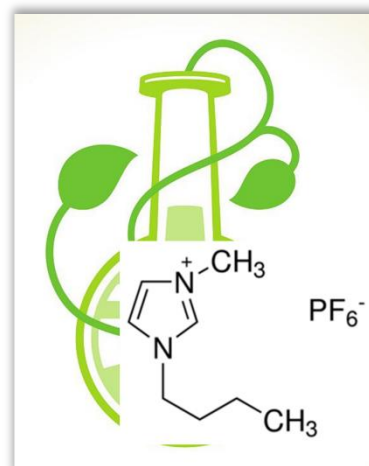


Figure 1: The obtained material (glass + IL= GILs) is a soft white powder.

### 3. Results and discussion.

X-ray diffraction patterns confirm the amorphous nature of every sample. Figure 2 shows the XRD patterns and any of them shows a sharp peak. From those figures we verify that the IL does not change the sample's amorphous nature.

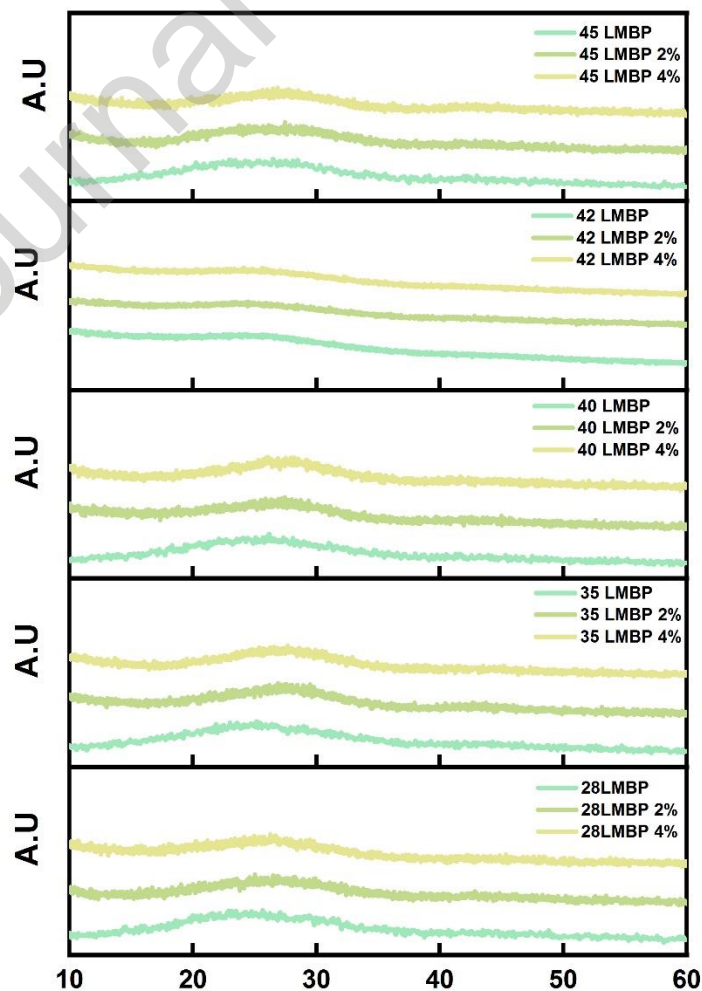


Figure 2: X-ray diffraction patterns of pristine glass, 2% and 4% GILs.

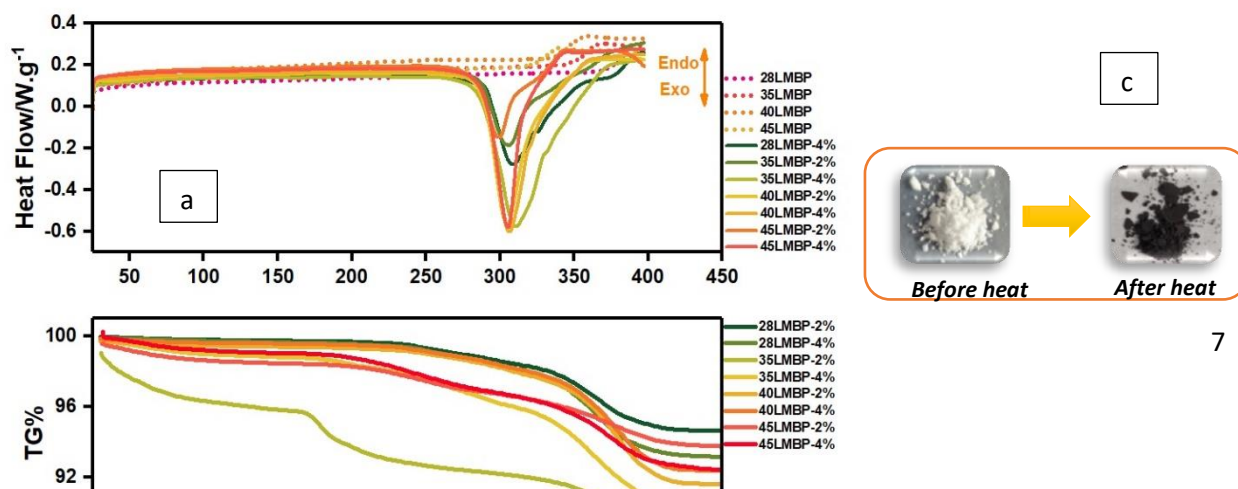
Density values reported in Table 1 are the average of three individual density measurements. From those values the molar volume ( $V_m$ ) and oxygen packing density (OPD= nominal oxygen mol number/ molar volume) are computed. We observe that both, the density and the OPD values decrease with the increase of lithium content, *i.e.*, the glassy matrix compactness diminishes due to the replacement of magnesium oxide by lithium oxide. Considering that the three-dimensional framework is built with oxygen polyhedral connected through its vertex, the OPD allows to explain the structure compactness variation caused by the incorporation of this modifier oxide ( $\text{Li}_2\text{O}$ ). The behaviour observed in the OPD reveals that lithium ions force the network into a spatial rearrangement in a more open skeleton.

Table 1: Molar Weight, Density, OPD,  $T_g$  and exothermic peak temperature.

<b>Li</b>	<b>Molar Weight</b> <b>(g.mol<sup>-1</sup>)</b>	<b>Density</b> <b>(g.cm<sup>-3</sup>)</b>	<b>OPD</b> <b>(mol O.dm<sup>-3</sup>)</b>	<b>T<sub>g</sub></b> <b>glass</b> <b>°C</b>	<b>GIL</b> <b>peak<sub>exothermic</sub></b> <b>°C</b>
<b>28</b>	<b>222.6</b>	<b>2.97</b>	<b>84.1</b>	<b>382</b>	<b>305- 308</b>
<b>35</b>	<b>221.0</b>	<b>2.97</b>	<b>84.6</b>	<b>359</b>	<b>305-310</b>
<b>40</b>	<b>219.9</b>	<b>2.94</b>	<b>84.1</b>	<b>349</b>	<b>305-306</b>
<b>45</b>	<b>218.9</b>	<b>2.87</b>	<b>82.7</b>	<b>332</b>	<b>305-306</b>

Figure 3 shows the TGA registers of each sample (pristine glass and GILs) in the range between room temperature and 500°C. In this figure, we observe that in between 25°C and 200°C none of the samples show a significant mass loss except for a small quantity of humidity. However, when the temperature rises the mass loss increases and, around at 350-400°C, the mass loss achieves a variation of around of 5% and 11% depending on the material composition. Thus, the GILs are not thermally stable beyond to 200-250°C. It has to be noticed that the initial colour of samples changes from white to grey after the heat treatment as figure 3b shows [5] observed something similar in composites and they concluded that it is very likely that the IL decomposes the substrate, and the resultant products are responsible for colour change. On the other hand, it was also explained that the oxides loss of oxygen when an IL is on the oxide surface [6, 7].

Figure 3a shows the heating DSC register of pristine glasses and GILs. Each pristine glassy sample shows its glass transition at around 350 °C. However, GIL samples show a strong exothermic peak near 300°C just some degrees before the mass loss, which, at a first glance, seems to mask the  $T_g$ . In order to clarify such loss of  $T_g$ , we repeated the heating scan using the DTA with high sensibility. Figure 4 shows the heating scan on the 28 LMBP and 45 LMBP as an example. In that figure we observe that the pristine glass  $T_g$  appears close to the end of the exothermic peak which is slightly deformed. In addition, a new  $T_g$  at a lower temperature is also evident. We assume that such new  $T_g$  is due to a different glassy phase formed on the surface as we will explain in detail afterward [8]. Additionally, figure 3c shows how the material changes its colour after the thermal treatment. Similar behaviours were previously observed when crystalline LTP and LATP was mixed with other ionic liquids [7].





b

Figure 3: a) DSC registers of pristine glasses and GILs; b) TGA of GILs and, c) GIL sample before and after heat treatment.

Additionally, figures 4 *a*, *b* and *c* show the  $T_g$  values of each sample, pristine glasses and each GILs. In this figure, we observe that the  $T_g$  values of pristine glasses are evident even in the Gils. However, the same figure shows that a new  $T_g$  is observed in each GIL around 100°C below of the glassy substrate's  $T_g$ . A similar behaviour has been reported in literature many times but, no interpretation of such behaviour has been explained as most of the time, it is assumed as the new  $T_g$  of the system is due to the difficulty to resolve both, the new one and the corresponding glassy substrate. [5, 9, 10]. N.H. RAY reported that the transformation temperature of an oxide network also depends on the tightness of its packing because, the more open the glassy network, the smaller the increase in the internal energy needed to achieve the mobility required for a rearrangement. Hence, the temperature needed for a transformation diminishes when a glassy network becomes less tightly packed [11]. In our composites, what it is observed from the results in Table 1 and in figure 3 is that not only the structure compactness is important but also, the chemical composition defines the transformation temperature.

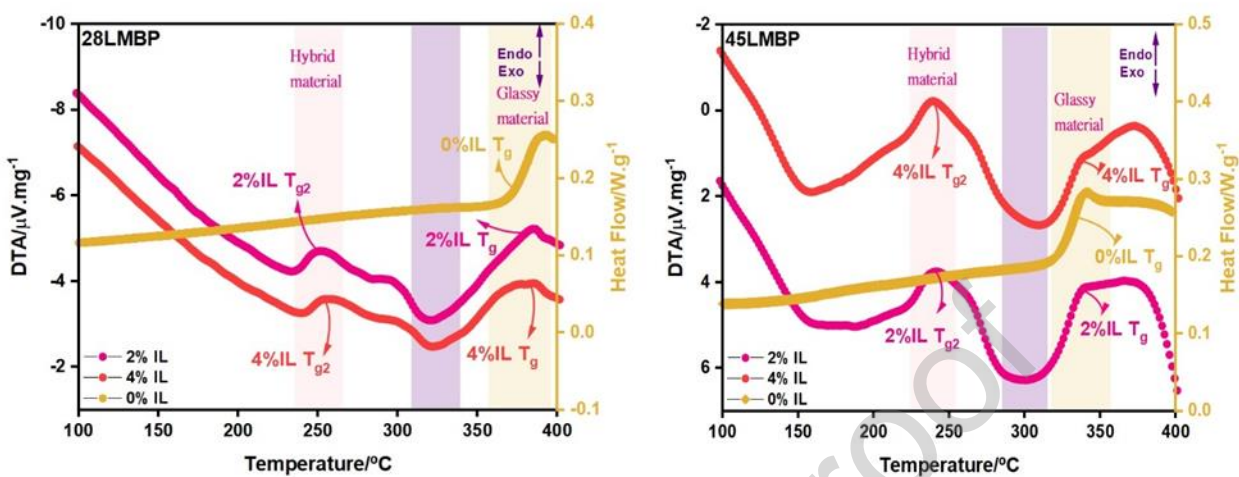


Figure 4:  $T_g$  values of LMPB and GILs.

FTIR spectroscopy is widely used as an effective tool to analyze the skeleton features of glasses. Figure 5 shows the spectra of the naked glassy substrates in the frequency range  $400\text{cm}^{-1} - 1300\text{cm}^{-1}$ . Here, we observe that the frequency of P-O bonds vibration changes with the number of bridging oxygen atoms. The broad band in between  $400\text{cm}^{-1} - 500\text{cm}^{-1}$  belongs to the bending vibrations of basic structural units of phosphate glasses while, the intense bands in  $1032\text{cm}^{-1}$  and in  $1045\text{cm}^{-1}$  suggest the presence of a high concentration of non-bridging oxygens which provides a large number of available sites for lithium ion hopping in the glassy matrix [4, 12]. In the same figure, the FTIR spectra of GILs with 2 and 4% of IL are compared. From those results, it is possible to observe that, firstly, the two mains [BMIM][PF<sub>6</sub>]-ionic liquid bands are in  $556\text{cm}^{-1}$  and  $624\text{cm}^{-1}$  (PF<sub>6</sub>-asymmetric- stretching and PF<sub>6</sub>-symmetric-stretching) [13] are present. Secondly, and more importantly, those bands assigned to BO become very intense compared to the naked glassy substrate while, those from the NBO are less intense. Therefore, we assume that the IL's cation forms new BO with the glass on the surface [14-18].

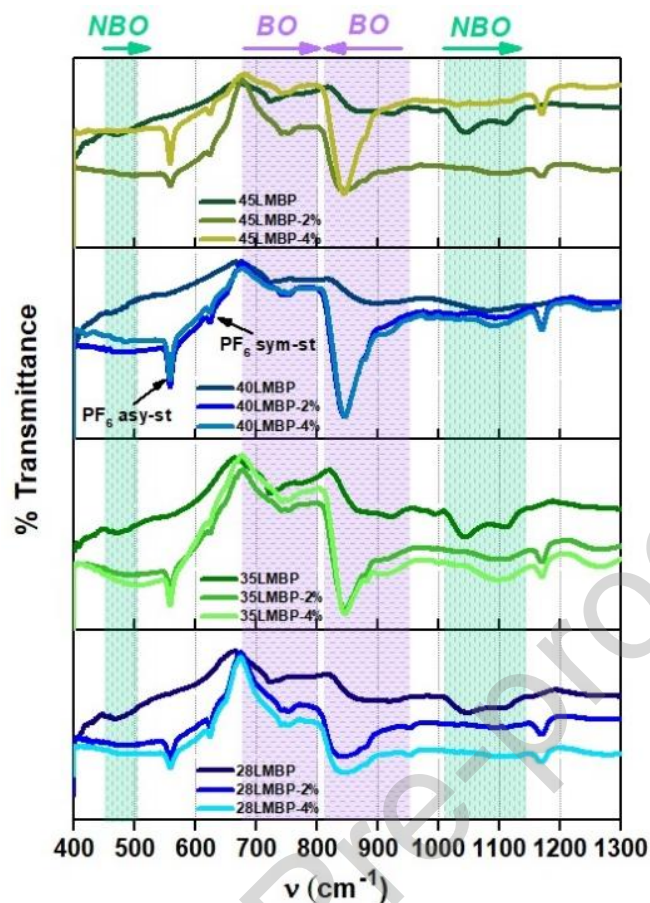


Figure 5: FTIR spectra of the naked glass and GILs. Frequencies highlighted belongs to P-O vibration in BO (purple) and NBO (green).

As we mentioned before, in 2004, A.J. Bhattacharyya and J. Maier presented a new kind of electrolyte called Soggy sand formed by mixing a liquid non-aqueous salt solution with a fraction of solid insulating particles (0.1M LiClO<sub>4</sub> with particles of SiO<sub>2</sub>; or Al<sub>2</sub>O<sub>3</sub>, or TiO<sub>2</sub>, radius 0.15μm approximately), they found a significantly increase in the material conductivity and ascribed that to the interfacial interactions and explained that the conductivity is enhanced due to a percolation path behaviour indicating that the anion salt is adsorbed while the lithium ion conductivity is increased when the particle solid surface is acidic enough [19]. At the same time, Kumar and Rodrigues tested the mix of ethylene carbonate and propylene carbonate with lithium hexafluorophosphate or lithium

tetrafluoroborate with two kind of inorganic nanoparticles: barium titanate and, alumina. They concluded that a space charge region in the colloid forms a phase that involved a high conductivity through a three-dimensional network that enhances that conductivity [20].

Therefore, to investigate the characteristics of the electrical conduction of the GILs studied in the present work, the impedance (Z) and the phase angle ( $\varphi$ ) as a function of frequency and temperature were measured. Considering that the electrical conductivity in glasses rises when the temperature increases, it is assumed that the Arrhenius-type equation [21] is the right one to analyse it:

$$\sigma_{dc} = \frac{\sigma_0}{T} e^{-E_a/kT}$$

where  $E_a$  is the activation energy of the conductivity process,  $\sigma_0$  is the preexponential factor and  $k.T$  have their usual meaning [22].

Figure 6a shows the temperature dependence of conductivity for the LMBP composition of the naked glasses and their GILs while figure 6b and c show some Nyquist plots of the GILs showing that, in every case, only one partial arc is obtained. This is an evidence that just the more conductive percolating phase is revealed which is also supported by the electrical formalism results presented in figures 11 and 12. The conductivity was measured on the powder-compressed pellets of the glasses as explained before. From this figure, it can be noticed that there is only one slope for each GIL; therefore, this can be interpreted as them having only one activation energy. However, the conductivity activation energy of GILs is considerably lower than the obtained for the naked glasses. An overall comparison among the conductivities at 323 K and their respective activation energies is presented in figure 6. In this figure, it is possible to observe that the addition of [BMIM][PF<sub>6</sub>] to the LMBP ionic powdered glass increases the total conductivity between 5 to 7 orders of magnitude without an apparent influence of the glassy composition substrate. Nevertheless, there is an unsolved question: which is

the real sample geometric factor (thickness/area)? Firstly, we use the macroscopic values of the composite to compute the total conductivity. The conductivity values of the GILs with 2 or 4 wt.% of [BMIM]PF<sub>6</sub> vary around 2 to 8.10<sup>-4</sup> S.cm<sup>-1</sup> in all the range of glassy compositions at 323K which is in the range of the conductivity values reported for the pure [BMIM][PF<sub>6</sub>] [19, 20]. Now, if we consider the total surface of particles considering the mean diameter reported in figure 10 and, a uniform surface distribution of IL on them, we obtain a thickness of around of 0.5 nm for Gil-4%, something enough to perform a percolated pathway for the charge carriers outside of the glassy particles and less uniform for 2%-Gils, justifying the more dispersed results observed in figure 7. This argument could explain why there is not much different among the conductivity values for samples with different lithium-ion content. Seems that only the IL is responsible for the electrical conduction. Nevertheless, it is important to note that we are using a small percentage of the ionic liquid and the resulting material behaves as a soft solid as show figure 8 where there is not leakage from the powder-compressed pellet which maintains its shape after the heating process up to 100 °C or evidence of any thermal behaviour of the [BMIM]PF<sub>6</sub> itself in the electrical measurements as expected from the calorimetric study showed above.

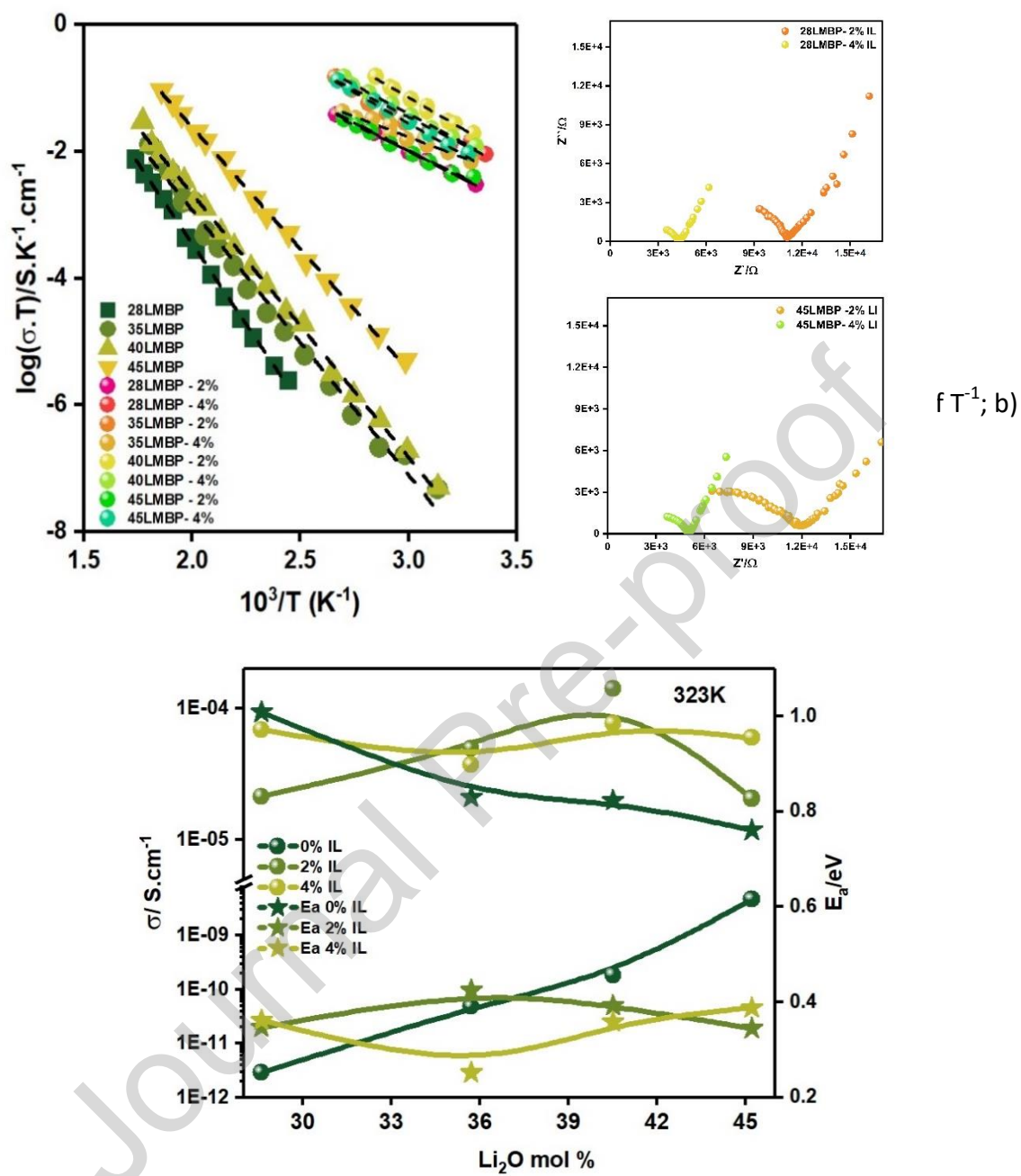


Figure 7: Conductivity isotherm (323 K) of LMPB and IL-LMPB.



Figure 8: The resulting material behaves as a soft solid material partially flexible.

A possible explanation of the huge conductivity increase is not evident at first glance because no salt was added. If the explanation were related to the rise in  $\text{Li}^+$  ion mobility that comes from the inside of the ionic glassy substrate, one would expect a straightforward correlation with the ion content in the glass. A first step to understand the electrical behaviour observed would be to analyse the glassy particle's surface charge through the Zeta potential. Figure 9 shows those results evidencing a large negative charge. Also, the diameter particle distribution is between 15 to 60  $\mu\text{m}$ . Considering the  $[\text{BMIM}]\text{PF}_6$  structure (figure 1) it is possible to assume that the total conductivity is majority given by the IL's anion, while the cation remains retained over the surface. Because of that, the  $\text{Li}^+$  contribution could be almost negligible despite the large conductivity variation observed [between the 28 LMBP and 45LMBP ( $10^{-12}$  to  $10^{-9}$   $\text{S}\cdot\text{cm}^{-1}$  at 323 K)]. Nevertheless, the substrate glassy composition manifests itself on the conductivity behaviour. To evidence this, figure 11 shows the conductivity spectra of 2 and 4 wt.% GILs joint to the naked glass with the highest conductivity (45LMBP) in which

the following is observed: i) at a high frequency, the higher the lithium content in the glassy matrix, the larger the conductivity dispersion; ii) at a middle frequency, the dc conductivity is governed by the IL content and the interaction with the surface of glasses with different chemical composition; and iii) at a low frequency, the higher the content of free IL's ions, the stronger the electrode blocking effect, something highlighting in figure 12 which shows the electrical results presented through the real part of the electrical permittivity as a function of frequency which evidence a large charge accumulation at the electrode at higher frequencies for GILs indicating higher ion mobility.

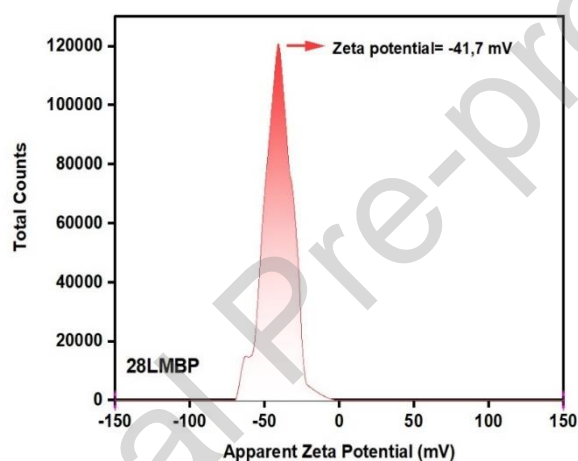


Figure 9: Zeta potential report at room temperature.

**Results**

Mean Size	: 53.49551(μm)	D(v,0.1)	: 6.17993(μm)
Mode Size	: 63.0484(μm)	D(v,0.5)	: 32.09693(μm)
Std.Dev.	: 57.4030(μm)	D(v,0.9)	: 133.94029(μm)
Geo.Mean Size	: 29.5686(μm)		
Geo.Std.Dev.	: 3.2668(μm)		

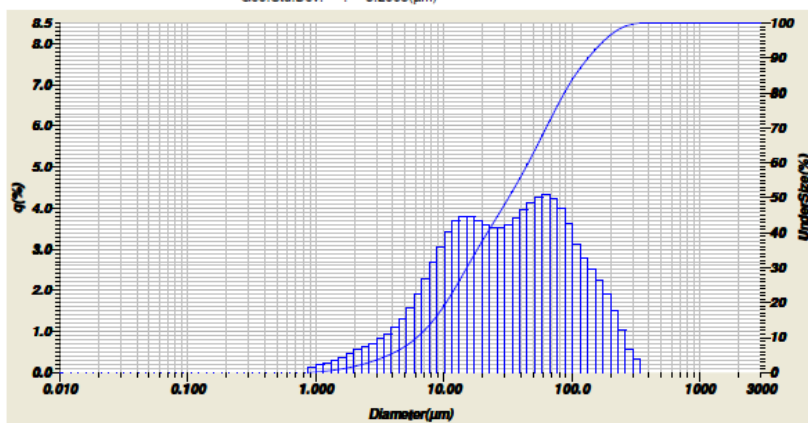




Figure 10: Particle size distribution.

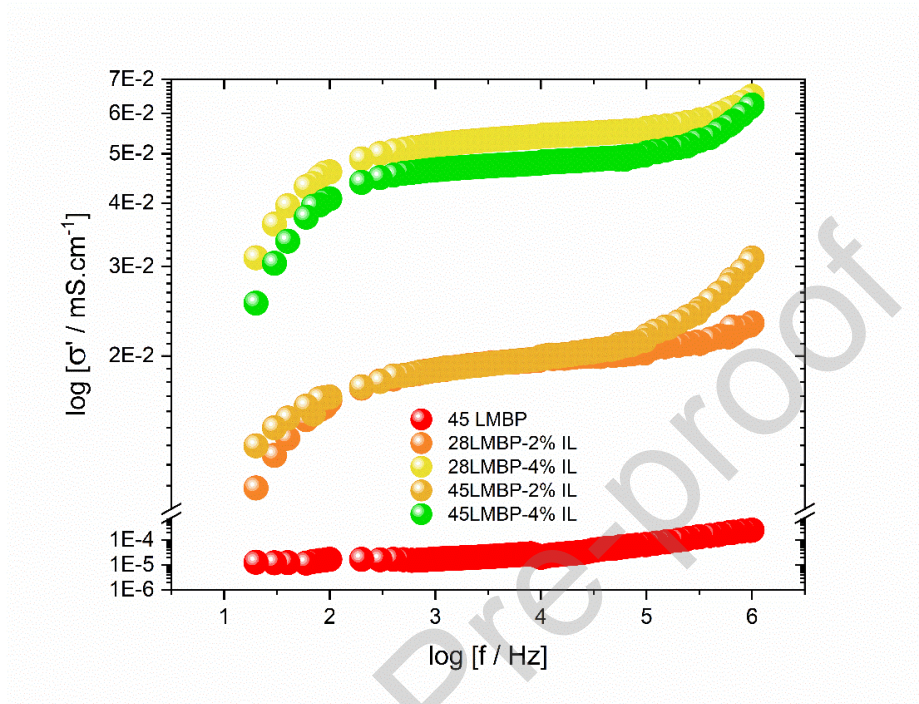


Figure 11: Real part conductivity spectra of 2% and 4% GILs and the naked glass with the highest conductivity (45LMBP).

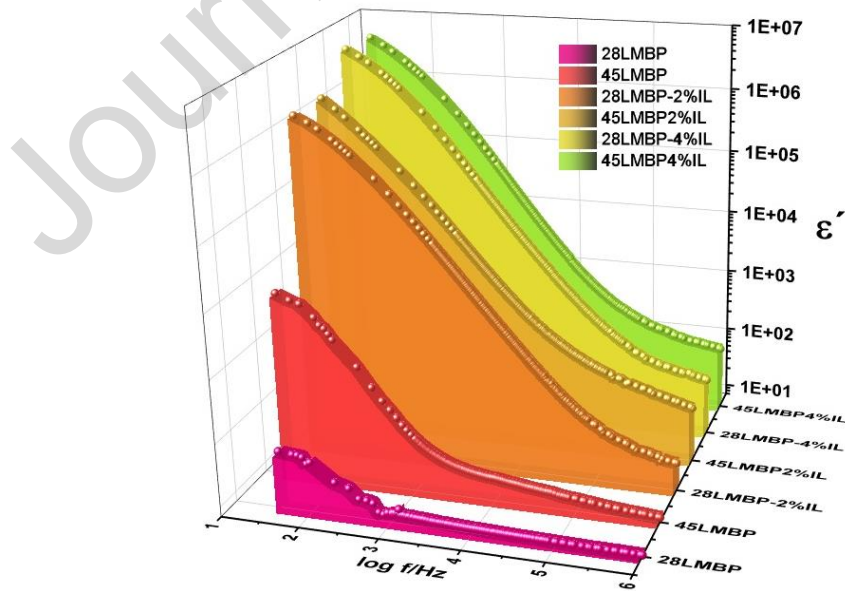


Figure 12: Real part of electrical permittivity as a function of frequency at 323 K of 2% and 4% GILs and the naked glass with the lower and the highest conductivity (28LMBP, 45LMBP).

## Conclusion

The interactions between the [BMIM][PF<sub>6</sub>] -ionic liquid- and the lithium phosphate glassy surface were studied and analysed through calorimetric, structural, and electrical results. Those results show that the [BMIM][PF<sub>6</sub>] mixed with this powdered ionic glass develop a soft solid conductor material. Such materials, which contain the ionic liquid in a low proportion (2 and 4%), were studied at microscopic level in order to understand how those interactions on the glassy particles surface act on the material's structural and electrical behaviour. This is a fundamental finding to consider the type and concentration of an additional lithium salt to develop a solid electrolyte for electrochemical devices.

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CRediT authorship contribution statement

**S. Terny:** Methodology, Validation, Formal analysis, Data Curation. **E. Cardillo:** Methodology, Validation, Formal analysis, Data Curation. **S. Barolin:** Resources, Data Curation. **M. A. Frechero:** Conceptualization, Methodology, Investigation, Resources, Data Curation, Writing - Original Draft, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

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**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:



S. Terny, E. Cardillo, S. Barolin, M. A. Frechero.