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Comparison of ionic conductivity of pure imidazolium nitrate and doped with a lithium nitrate salt in liquid and gel forms as potential electrolytes.

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Abstract: Current electrolytes for electrochemical energy storage devices are made of solvent which often present problems of flammability, corrosion and high toxicity. Ionic liquids and mixtures with metal salts are proposed as a good selection for more safety electrolytes due to their properties as, among others, non-flammability, negligible vapour pressure, high ionic conductivity and wide electrochemical window. In this work, electrical conductivity of solutions of the ionic liquid 1-Ethyl-3-methylimidazolium nitrate ([EIm][NO_3]) with lithium nitrate salt in three different concentrations has been analysed for liquid and gel states. Temperature and salt concentration dependences of electrical conductivity have been studied for liquid and gel states. As expected, an increase of conductivity with temperature and a decrease whit salt concentration were observed, except for the case of gel [EIm][NO_3] with salt concentration of 0.5 m which shows a little increase of conductivity compared to the pure gel. Comparison of conductivity of the liquid and gel states shows a significant increase for gel state at low concentrations of the added salt.

Keywords: electrical conductivity, electrolytes, gel, imidazolium

1. Introduction

The increasing demand for batteries has led industry and academy to focus on improving the performance, safety and cost of lithium battery technology. Replacing the flammable electrolytes used in current batteries with non-flammable compounds, as for example ionic liquids (ILs) doped with inorganic salts containing relevant metals for this electrochemical application [1,2] can be an important step to achieve these improvements.

ILs are nanostructured green compounds considered as a new class of solvents, whose properties can be appropriately tuned (designer solvents) choosing combination of cation and anion from the large number of currently known IL moieties.

Recent studies suggest the possibility of using sol-gel electrolytes [3] in electrochemical devices to improve the safety of the electrolyte and make easy the manipulation, although the behaviour of some key properties as ionic conductivity after gelation are not deeply studied, finding in literature some contradictory results.

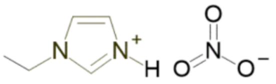
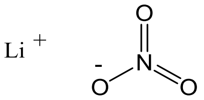
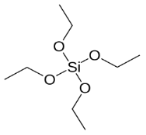
In this work, the effect of gelation and the influence of the lithium salt doping of the ionogel of the ethylimidazolium nitrate ionic liquid are analysed in terms of ionic conductivity against temperature.

2. Materials and Methods

2.1. Chemicals

Solutions of the IL [EIm][NO_3] with Lithium salt ($LiNO_3$) via stirring mixing at three different concentrations ((0.5, 1 and 3) mol·kg^{-1}) were prepared. Chemical Structure and further identification of chemical compounds (CAS Number, Molecular Weight…) can be found in Table 1. Furthermore, detailed information of mixtures can be found in Table 2.

Table 1.-Identification of Chemicals used in this work.

Name	Molecular Weight (g·mol^{-1})	Structure	CAS number	Provenance
Ethyl Imidazolium Nitrate	159.14		[EIm][NO_3] 501693-38-5	Iolitec
Lithium Nitrate	68.946		$LiNO_3$ 7790-69-4	Sigma Aldrich
Tetraethoxysilane	208.33		TEOS 78-10-4	Sigma Aldrich

[EIm][NO_3]- Lithium Salt mixtures were dried via vacuum procedure for 24-48 hours in order to remove water content. The residual quantity of water was measured using a Karl Fisher titrator and quantities of water lower than 100 ppm were obtained.

Table 2.- Molality of the studied samples and mass of pure metal salts per 100 g of pure IL.

[EIm] [NO_3] + $LiNO_3$	Molality /molt$_{salt}$·kg$^{-1}_{[EIm][NO3]}$	Pure salt mass /g (100g of IL)$^{-1}$
PURE	---	---
Li 0.5 m	0.5	3.5
Li 1 m	1	6.89
Li 3 m	3	20.68

Gelation Routes

A main procedure to sol-gel route in order to prepare gel samples was carried out, using an adaptation of the method described by Garaga et al. [4]. A brief description of the selected method is the following:

- The volume proportions of sample mixtures are 3 parts Of EtOH, 0.428 of TEOS and 1 of [EIm][NO_3] (or mixture), then were stirred in a round flask at least during 60 min.

- After that, they were transferred to a vial, where the mixture was stored in a furnace at 40 °C until ethanol was completely evaporated (7-8 days).

3. Experimental

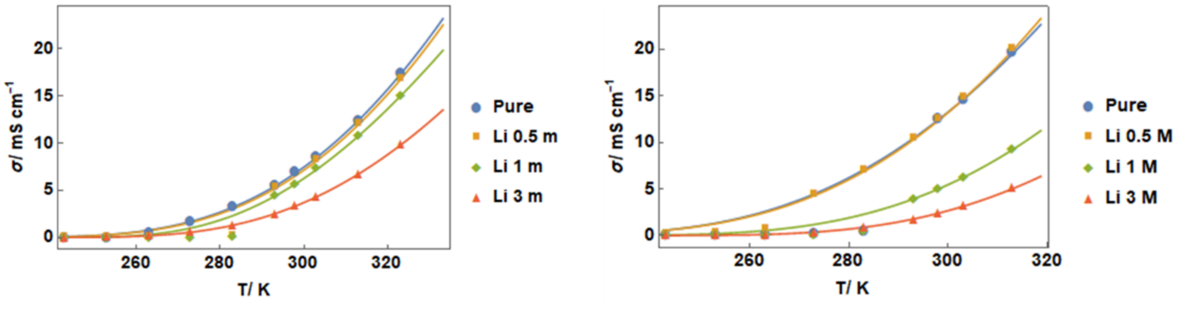
Electrical conductivity

With the purpose of obtain electrical conductivity (σ) a conductimeter GLP31 from CRISON was used at a constant frequency of 500 Hz. The resolution of this conductivity meter is better than 1% of the measured value; the minimum and maximum values registered by CRISON GLP31 are 0.2 $\mu S\cdot cm^{-1}$ and 100 $mS\cdot cm^{-1}$, respectively. The probe is formed by two parallel flat platinum plates which can take measurements in the case of liquid or gel samples in a temperature range from (243 to 323) K. A calibrated Julabo F25 thermostat was used to control the temperature of the sample; the error in the temperature was lower than 0.1 K. These measurements need to be taken in an isothermal regime, so the time spend in every measurement was, at least 15 min while there was no phase transition. When phase transition takes places, the time spent on the measure was more than 30 min.

4. Results

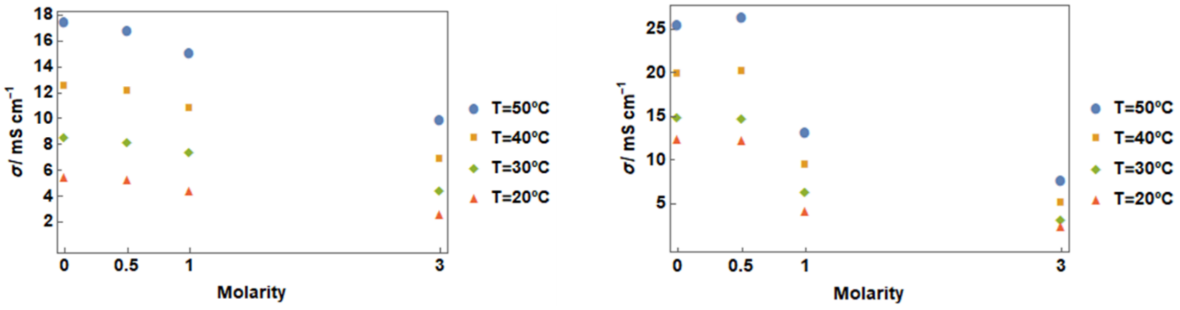
Fig.1 shows the ionic conductivity of IL-salt mixtures versus temperature of (a) liquid form, (b) gel form. It can be seen an increase of conductivity with temperature for all samples. The temperature dependence of the ionic conductivity of all the samples was found to be well described by Vogel-Fulcher-Tamman (VFT) equation [5]. On the other hand, a clear decrease of conductivity with the salt concentration in liquid state is also observed, and different behaviour can be observed for gel form (Fig. 1.b), characterized by an increase of conductivity until a maximum value (around 0.5 mol_{salt}/kg), followed by a decrease with salt addition.

The increase of conductivity for the lowest studied concentration of salt addition in gel state can be clearly noted out in Fig. 2, which shows the conductivity vs molality curves for different temperatures.



(a) (b)

Figure 1. Electrical conductivity vs temperature measured in cooling ramp for (a) liquid and (b) gel form. Lines in figure correspond to VFT fitting curves in liquid and in gel form.



(a) (b)

Figure 2. Electrical conductivity vs temperature in cooling ramp for (a) liquid and (b) gel states.

This behavior agrees with Garaga et. al. [4] who found an enhancing of ionic mobility after gelation using silica micro-particles, although for our knowledge, studies about the behavior of conductivity with the salt addition in gel forms have not been performed.

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