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Silica-Polymer Ionogel for Energy Storage Applications †

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Abstract: Ionic Liquids (ILs) are composed of ions, usually an organic cation with an organic or inorganic anion, with melting point below 100 °C, and in most cases below room temperature. These compounds exhibit important and characteristic properties such as high ionic conductivity, good thermal and electrochemical stability and low toxicity and flammability. Subsequently, ILs have been studied as promising substitutes for conventional electrolytes for electrochemical applications, both as bulk liquids or confined in a polymer matrix, commonly known as ionogels, which have the advantage of no leaking, enhancing safety and manipulation during device assembly. For this work, the ionogel of the IL 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_2C_1Im][TFSI]) has been synthesised by polymerization of Tetramethyl orthosilicate (TMOS) and Dimethyldimethoxysilane (DMDMS). Thermal analysis of the pure ionic liquid and electrochemical response of the ionogel were studied in comparison with the corresponding bulk IL by using differential scanning calorimetry (DSC), thermogravimetry (TGA) and broad band dielectric spectroscopy (BBDS), respectively.

Keywords: ionic liquids; ionogels; DSC; TGA; BBDS; conductivity

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1. Introduction

The substantial increase in energy and resources consumption caused by rapid growth of worldwide population, fossil fuel reserves depletion, greenhouse gas emissions and global warming are some of the biggest challenges that humanity is facing in the present day. The most promising solution is brought by renewable energies, but it does frequently come at a cost: intermittency. Therefore, energy storage has become an indispensable piece of the puzzle for an effective sustainable transition.

Among the finest energy storage devices are lithium metal batteries (LMB) and lithium-ion batteries (LIB). However, they still face some difficulties, being the ones associated with electrolyte performance the focus of this work.

Liquid electrolytes (LE) present performance disadvantages due to parasitic reactions between lithium anode and LE, provoking a decrease in Coulombic efficiency and shortening LMB's lifespan. Moreover, leakage risk, insufficient thermal stability, and dendrite formation, which can lead to battery short circuits, pose an important safety hazard [1]. One of the most promising LE are ionic liquids (IL), which are defined as molten salts whose melting point is below 100 °C. These compounds present outstanding properties for the electrochemical industry, such as high ionic conductivity, good thermal stability, low flammability, wide electrochemical window, etc. However, as liquids, they still face leakage risk [1].

Aiming to ensure battery safety, solid electrolytes (SE) have been developed. These electrolytes possess the advantage of no leakage risk and prevent dendrite formation. Nevertheless, they lose against LE in terms of ionic conductivity and ease of manufacture [1].

These two types of electrolytes find common ground in ionogel electrolytes (IG). Ionogels consist of immobilization of IL in a polymer matrix, therefore are situated midway between liquid and solid electrolytes, combining the advantages of the two worlds. IG provide a wider temperature range of function compared to LE, are inert towards the metallic lithium and can prevent dendrite growth while allowing good contact between electrode and electrolyte and presenting higher ionic conductivity than SE [2].

The aim of this study is to extend knowledge about ionogels and their opportunity as promising electrolytes for the electrochemical industry. Hence, the conductive behaviour of an ionogel based on 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMimTFSI) synthesized by sol-gel method in comparison with the priscine IL is analysed in this work.

2. Materials and Methods

2.1. Chemicals and Gelation Process

The IL 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (cas number 174899-82-2), commonly referred to as EMimTFSI, was selected for this study. Even though this IL has been reported to be a hydrophobic compound [1], it has been dried in a vacuum chamber for at least 48h at room temperature to ensure minimal water content and other impurities.

The ionogel based on this IL has been synthesized via the sol-gel method, following a similar approach to Chen et al. [3]. Tetramethylorthosilicate (TMOS) and Dimethyl Dimethoxysilane (DMDMS) have been selected as silica precursors and formic acid (FA) as catalyst.

The synthesis procedure was the following: firstly, TMOS was mixed with DMDMS in a molar proportion 0.7:0.3 and stirred for 10 min. Afterwards, EMimTFSI is added in a relation 0.5[0.7:0.3] (EMimTFSI[TMOS:DMDMS]) and stirred again for another 10 min before the addition of FA and finally stirred for 2 min more. Lastly, the ionogel was aged for 6 days at room temperature, the first 2 days it is covered with a lid, followed by another 4 days uncovered.

2.2. Differential Scanning Calorimetry (DSC)

A Differential Scanning Calorimeter (DSC) Q2000 (Waters-TA Instruments, New Castle, DE, USA) was used with hermetically sealed aluminium pans, sample masses ranging from 5 to 8 mg; experiments were performed under nitrogen atmosphere. One Heating-cooling cycle between −80 °C and 50 °C was performed at rate of 5 °C/min, with an initial ramp from room temperature to 125 °C at 40 °C/min, with a 45-min isothermal step at 125 °C to eliminate potential volatile impurities. Transition temperatures of the pure IL were determined at the onset of peaks observed in the DSC curves during the reheating and recooling phases. The transition temperatures were estimated with a 2 °C uncertainty at a 95% confidence level [4].

2.3. Termogravimetry Analysis (TGA)

To study the short-term thermal stability of pure IL, a Mettler Toledo DSC/TGA1 instrument in dynamic mode, with a heating rate of 10 °C/min and a purge gas flow of 20 cm^3/min, covering a temperature range from 50 °C to 800 °C under a nitrogen atmosphere was used. Samples weighing over 40 ± 1 mg were placed in an open platinum pan for analysis [5,6].

Since it has been demonstrated multiple times that the onset temperature (t_{onset}) tends to overestimate the working temperature of the compound [5,6], several models have been proposed to obtain a more accurate operating temperature. Wooster et al. [7] established a method to estimate the maximum operating temperature from dynamic scans using the Equation (1):

$$T_{0.01/10\mathrm{h}} = 0.82 \cdot T_{(\mathrm{dw}/\mathrm{dT}\neq 0)} \tag{1}$$

where $T_{(dw/dT\neq 0)}$ corresponds to the temperature (in Kelvin) at which the first derivative of the weight loss curve with respect to T is not equal to zero.

2.4. Broad Band Dielectric Spectroscopy (BBDS)

In order to obtain the ionic conductivity of both bulk IL and the ionogel, a broad band dielectric spectroscopy was carried out. For this, an Agilent RLC precision meter HP 4284A (Agilent Technologies, Santa Clara, CA, USA) with a precision of 0.05% was used; coupled with a climate chamber (Memmert ICP400, Schwabahc, Germany) for temperature control. The sample was fixed inside a two-electrode Swagelok cell ensuring good contact between electrodes and electrolyte (Figure 1) [8].

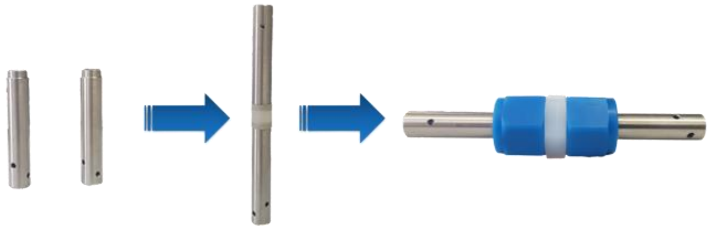

Figure 1. Scheme of the assembly of a two-electrode Swagelok cell.

The selected temperature range was 0 °C to 50 °C and the frequency sweep was conducted between 20 Hz and 1 MHz with logarithmic step to ensure that the measurement includes the ohmic region. With the aim of obtaining the ionic conductivity (σ), the imaginary part of the dielectric constant (ε'') was presented against the frequency (ω) and fitted to the Equation (2) with a tolerance for the slope of −1 ± 0.02 [2,8].

$$\log(\varepsilon'') = \log\left(\frac{\sigma}{\varepsilon_0}\right) - \log(\omega) \tag{2}$$

3. Results

3.1. Liquid Range of the Pure IL

Figure 2a shows the DSC curve of pure IL obtained during the heating and cooling process at 5 °C/min. Upon cooling an exothermic peak is observed corresponding to the crystallization of the IL with an onset temperature of −50 °C. Additionally, a cold crystallization, exothermic process, at −53 °C, followed by a characteristic endothermic peak at −19 °C associated to melting can be observed clearly upon heating.

Figure 2b shows the thermogravimetric curves corresponding to the dynamic study of EMim TFSI, showing the mass loss curve and its corresponding derivative. It can be observed that this compound undergoes the mass loss process in a single step (one peak in the DTG), as previously observed by other authors [9,10]. Furthermore, we can determine the characteristic thermogravimetric parameters of the IL, t_{onset} (represents the beginning of the mass loss process), t_{endset} (represents the ending of the mass loss process), W_{onset} (mass loss percentage at onset temperature), t_{1st} (maximum at DTG curve) and t_{wooster} (1% degradation in 10 h), presented in Table 1, which are similar to those reported by other authors for this same IL [9,10].

Table 1. Characteristic thermogravimetric properties of EMim TFSI.

t_{onset}/°C	t_{endset}/°C	W_{onset}/%	t_{1st}/°C	$t_{wooster}$/°C
440	490	82	472	285

Additionally, a discrepancy of 185 °C can be observed between the t_{onset} and the $t_{Wooster}$, highlighting the need for isothermal studies. These studies involve maintaining a constant temperature for a specified period to analyze the percentage of mass loss at a given temperature, which, as demonstrated by other authors, will be significantly lower than the t_{onset}.

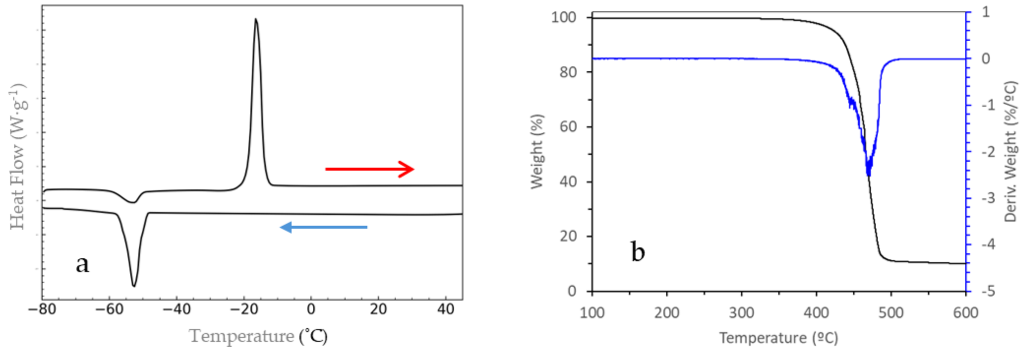

Figure 2. DSC curves at 5 °C/min (Exo down) (**a**) and TG (black) and DTG (blue) curves of pure EMim TFSI (**b**).

Then, it can be concluded that this IL has a large liquid range, between its melting temperature and its thermal stability temperature, between −19 °C and 280 °C, enough to be used as electrolyte in high-temperature solid state batteries.

3.2. Ionic Conductivity

The comparison between the ionic conductivity of bulk EMimTFSI and the ionogel EMimTFSI 0.5[0.7:0.3] is shown in Figure 3 and Table 2. Results of bulk IL are in good agreement with previously published literature [3], presenting conductivities of several mS/cm. In the case of the ionogel, it drops approximately one order of magnitude. However, as it is still close to 1 mS/cm at ambient temperature, it is considered adequate for electrochemistry applications.

Both the liquid and gel samples exhibit a similar trend in ionic conductivity with increasing temperature. As expected, conductivity rises with temperature, which is related to the decrease in viscosity, but the increase is more pronounced in the liquid sample [11,12].

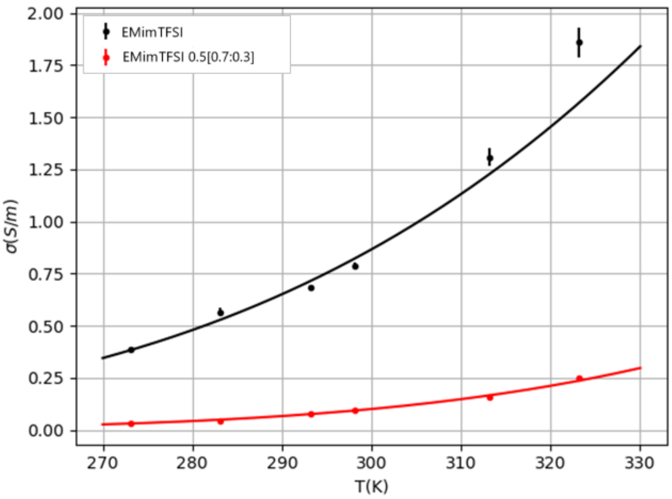

Figure 3. Ionic conductivity vs temperature for liquid EMimTFSI and ionogel EMimTFSI 0.5[0.7:0.3] with their fitting to the Arrhenius equation.

Table 2. Ionic conductivities (in $\mathrm{mS \cdot cm^{-1}}$) of bulk EMimTFSI and EMimTFSI 0.5[0.7:0.3] for different temperatures.

Temperature (°C)	EMimTFSI	EMimTFSI 0.5[0.7:0.3]
0	3.893(48)	0.3204(58)
10	5.66(18)	0.466(12)
20	6.82(12)	0.766(21)
25	7.87(14)	0.957(32)
40	13.09(44)	1.584(54)
50	18.59(71)	2.506(86)

This behavior of ionic conductivity with temperature is explained by the Arrhenius Equation (3), being σ_∞ the limit of the ionic conductivity when the temperature (T) tends to infinity, R the ideal gas constant and E_a the activation energy. The fitting of the obtained results to the Arrhenius equation is shown in Figure 3, and its parameters are presented in Table 3. The increment of the activation energy with the gelation of the compound is consistent with the decrease in conductivity.

$$\sigma = \sigma_\infty \exp(-\frac{E_a}{RT}) \tag{3}$$

Table 3. Fitting parameters of the Arrhenius equation for bulk EMimTFSI and ionogel EMimTFSI 0.5[0.7:0.3].

Compound	σ_∞ (kS $\cdot$ m^{-1})	E_a(kJ $\cdot$ mol^{-1})
EMimTFSI	3.44(59)	2.067(41)
EMimTFSI 0.5[0.7:0.3]	14.9(3.0)	2.970(48)

4. Conclusions

This work is aimed to analyze the changes on the conductive behaviour of an ionogel synthesized by sol-gel method in comparison with the bulk ionic liquid. Additionally, the transition temperatures and thermal stability of pure IL EMimTFSI were also analyzed to ensure the liquid state in all the temperature range studied. The main conclusions are summarized as follows:

- The selected compound exhibits excellent thermal properties, with a melting point at −19 °C and thermal stability higher than 250 °C.

- As expected, the ionic conductivity of the liquid sample increases with temperature, displaying values well-suited for the intended application.
- Gelation reduces the ionic conductivity, but it remains adequate for energy storage applications.

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