

Proceeding Paper

# Ionogels: Polimeric and Sol-Gel Silica Nanoscaffolds of Ionic Liquids as Smart Materials †

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**Abstract:** The purpose of this work is to check the viability of mixtures of ionic liquids and lithium salt as electrolytes in Li- batteries. Firstly, the determination of the thermo-electrical properties of liquid mixtures of the ionic liquid N-butyl-N-methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide [BMPyr][TFSI] with [Li][TFSI] salt at different concentrations was performed. Additionally, these results were compared with the corresponding ionogels of these mixtures designed by two different gelation methods, one of them using Poly (vinylidene fluoride) (PVDF) as a supporting matrix and the other one using a silica matrix.

**Keywords:** electrolyte; polymer; energy storage; ionic liquids



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## 1. Introduction

The energy transition towards forms of production and storage that allow complete sustainability and decarbonisation of the economic cycle is, at once, an urgent requirement of the current climate situation. The unstoppable energy transition process towards an increasingly sustainable and climate-neutral model based on renewable energies is related to the efficient storage and sustainable consumption of this energy. This is a huge worldwide challenge involving the scientific community, politicians and all of society [1].

Regarding efficient energy storage, as a result of the development of 4th and 5th generation recyclable batteries, new materials are one of the critical topics in current studies, especially for electrolyte and electrode designs [2]. In recent years, research related to new electrochemical materials has experienced great progress. Some of the most promising materials are ionic liquids (ILs), which are organic salts formed by a cation and an anion whose melting point is below 100 °C. The tuneability of the properties of ILs from the infinitely combinable anions and cations, and the possibility of introducing functional groups in their alkyl chains, make these fluids appropriate for many industrial applications, for example, electrolytes in mixtures of ILs and inorganic salts, mainly lithium salts [3,4].

ILs confinement in a matrix improves handling while reducing the possibility of spillage and the resulting grave consequences. This immobilization of ILs (or mixtures with inorganic salts) is known as gelation, and the resulting material is denominated as ionogel or ionic gels.

In this work, a pure IL (1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide) in liquid and gel state, obtained by two different routes, is analysed as a functional battery electrolyte in terms of broad band dielectric spectroscopy (BBDS). The effect of lithium salt addition to liquid and gel samples was also studied in terms of ionic conductivity.

## 2. Materials and Methods

### 2.1. Chemicals

For performing this work, an IL and a lithium salt with common anion, in liquid and gel form were selected. Table 1 shows a short description of the compounds used, molecular mass, short name, CAS identification number and provenance.

**Table 1.** Identification of chemicals used in this work.

Name	Molecular Mass (g·mol <sup>-1</sup> )	Short Name	CAS Number	Purity Supplier
Ionic liquid: 1-butyl-1methyl-pyrrolidinium bis(trifluoromethanesulfonyl)imide	422.41	[BMPyrr][TFSI]	223437-11-4	>99% IoLiTec
Salt: Lithium bis(trifluoromethanesulfonyl)imide	287.09	[Li][TFSI]	90076-65-6	>99% Sigma Aldrich
Gel Precursor: Poly(vinylidene fluoride)	Mw ~ 534,000	PVDF	24937-79-9	Alfa Aesar
Gel Precursor: Tetramethyl orthosilicate	152.22	TMOS	681-84-5	98% Sigma Aldrich
Gel Precursor: Dimethoxydimethylsilane	120.22	DMDMS	1112-39-6	98% Sigma Aldrich

### 2.2. Gel Preparation

The first method is based on a solution of TMOS and DMDMS, which, in the presence of formic acid (FA), hydrolyses Si-O bonds, forming a 3D network in whose pores the IL is immobilized. This gelation method was based on the route devised by Brachet et al. [5], which can be summarized in three steps:

- Firstly, TMOS and DMDMS with a molar rate 0.65 to 0.35 are mixed and stirred for 10 min.
- Secondly, [BMPyrr][TFSI] at a 0.8 molar rate is added to the previous mixture and stirred for an additional 10 min.
- Lastly, formic acid in a molar proportion of 3.3 is added, left in agitation for 2 min and finally, introduced in a Teflon mold.

The gel must remain covered for 2 days, and then left uncovered for another 5 days to achieve an accurate gelation. The gel may contain some impurities (precursors rest and other volatile products formed during the gelation), so a purifier vacuum process must be performed.

The second gelation method is based on PVDF, which is a nanometric powder that is mixed with dimethylformamide (DMF), whose only purpose is to triggers the gelation reaction [6]. The process followed to obtain the precursor matrix is:

- Mix 8% PVDF in mass with 92% DMF and stir for 3 h.
- Next, considering that PVDF is the hosting matrix (and DMF is only a solute to trigger the gelation process), the mass of PVDF vs IL is adjusted again, in mass proportions of 13% of PVDF and 87% of IL, and then mixed for 3 min and kept in a Teflon mold.

The gel must remain covered for 2 days and then remain open to the environment for another 5 days until the major part of the DMF has evaporated. To finish the gelation process, the gel is placed in a vacuum for 1 h, and then after, a heat treatment is performed, which consists of keeping the gel in a vacuum at 110 °C for 40 min. When the heat treatment is completed, the gel must be kept in a vacuum for a minimum of 24 h to evaporate the impurities produced by the gelation process.

### 2.3. Experimental Procedure

The electrical properties of the pure IL and mixtures were analyzed through complex impedance spectroscopy in a frequency range of 20 Hz to 1 MHz and a temperature interval of 273–323 K by using a RLC HP 4284A precision meter from Agilent, working with 8610 selectable frequencies between the selected frequency range. The basic accuracy of HP 4284 A is better than 0.05%. The applied sinusoidal voltage presents an amplitude of 0.2 V. This RLC precision meter presents 20 impedance parameters, each one with its own measurement range, i.e., G and B (conductance and susceptance, respectively), with a measurable range between 0.01 nS to 99.9999 S, while for  $Z'$  and  $Z''$  (resistance and reactance, respectively), the measurable range is between 0.01 m $\Omega$  to 99.9999  $\Omega$ .

A Swagelok coin cell with two parallel electrodes of stainless steel (4 mm radius and 1 mm of thickness) was used for experimental measurements. The short circuit compensation of the cell and its correction coefficient were considered to eliminate the effect of stray capacitance during the evaluation of the frequency-dependent values of complex dielectric function [7].

A calibrated Julabo F25 thermostat was used to control the temperature of the sample; the uncertainty of the temperature was lower than 0.1 K. All of the measurements were performed using an isothermal regime.

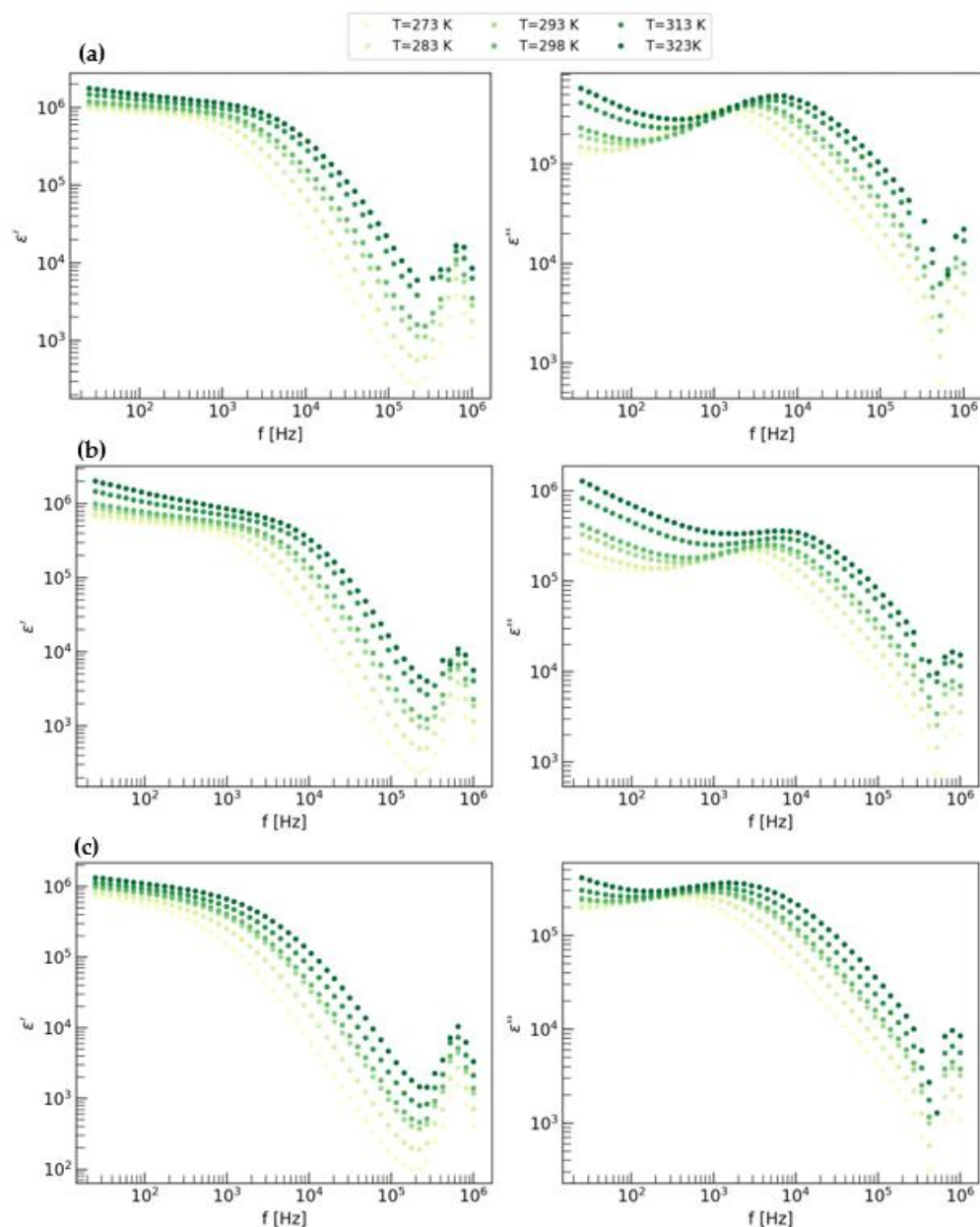
### 3. Results

The real dielectric constant ( $\epsilon'$ ) spectra (Figure 1) differs in two characteristic regions in the studied frequency range, separated by a frequency around 2 kHz. At the low frequency range,  $\epsilon'$  decreases linearly over five orders of magnitude, with a slope greater than the unity as the frequency increases. The great response of  $\epsilon'$  at low frequencies is due to the electrode polarization contribution (EP). This effect represents the formation of the double electric layer (EDL) at the interface of the dielectric material and the electrode, due to the accumulation of ions and free charges [8].

When the frequency increases, the dipole rotational contribution becomes greater and  $\epsilon'$  follows the Maxwell Boltzmann statistics [9]. As the frequency increases, the dielectric response decreases due to the difficulty of the ions to follow the electromagnetic vibrations. At a fixed frequency, the  $\epsilon'$  response enlarges as the temperature increases, which reveals that the concentration of the induced ions contributing to the formation of the EDL becomes greater with increasing temperature [10].

Regarding the imaginary part of the dielectric constant ( $\epsilon''$ ), it shows a plateau-like measurement at low frequencies with a maximum that increases with temperature, followed by a linear decrement in a double-logarithmic scale. The decrement slope is approximately  $-1.00$ , which is characteristic of the ohmic region (the current density has a linear response with the applied electric field) [11]. The ohmic region varies as the temperature increases, since the initial frequency moves to greater frequencies. The plateau at low frequencies is caused by non-aligned lines of the ions and the applied electric field [12].

When the temperature is over 40 °C, the ohmic region of pure [BMPyrr][TFSI] is outside of the studied region, so it is not possible to obtain the ionic conductivity by the applied method, making it necessary to enlarge the frequency range to over 1 MHz.

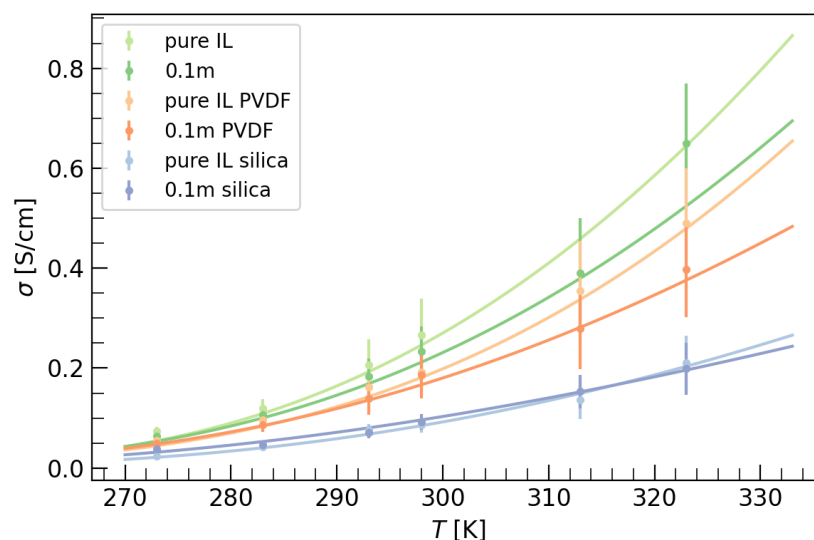


**Figure 1.** Real and Imaginary dielectric constant against frequency. (a) Pure [BMPyrr][TFSI]; (b) [BMPyrr][TFSI] PVDF gel. (c) [BMPyrr][TFSI] silica gel.

Every compound shows an increasing conductivity as temperature increases (Figure 2). When temperature rises, the viscosity of the compound becomes lower; thus, the ions can flow easily giving greater transport properties.

The salt addition triggers a decrease in ionic conductivity due to a reduction in fluidity (increase of viscosity with salt addition). The decrease in conductivity is due to the increasing formation of  $Li(TFSI)_2^-$  as a result of the Li ions coordinating with  $TFSI^-$  anions [13].

The gelation provokes a diminished conductivity at every temperature and salt concentration. The decrease in ionic conductivity is caused not only by ion concentration reduction in gelation, but also by the mobility decrease that could be due to the nanoconfinement in the matrix scaffold (Figure 2).



**Figure 2.** Ionic conductivity against temperature.

The silica gel ionic conductivity is lower than PVDF gel, becoming half at 50 °C (Table 2). This is because on silica gels, the IL proportion is much lower than PVDF gels (0.8 molar rate in silica gels, 83% mass in PVDF gels), which reduces the ions' proportion and conductivity.

**Table 2.** Compound ionic conductivity at different temperatures.

T [°C]	Pure IL	0.1 m	Pure PVDF	0.1 m PVDF	Pure Silica	0.1 m Silica
0	0.0735(90)	0.0642(63)	0.0546(51)	0.0495(59)	0.0240(22)	0.0388(37)
10	0.0119(90)	0.106(13)	0.096(13)	0.086(13)	0.0425(51)	0.0473(53)
20	0.207(51)	0.183(36)	0.162(26)	0.139(32)	0.076(12)	0.071(11)
25	0.266(73)	0.233(51)	0.192(43)	0.186(47)	0.087(16)	0.092(16)
40		0.39(11)	0.355(99)	0.279(81)	0.137(39)	0.153(34)
50		0.65(12)	0.49(11)	0.397(95)	0.211(54)	0.199(52)

Both liquid and gel PVDF and silica samples follow a VFT behavior [14], which suggests that in both states, the dynamic structure is similar and the energy process of conduction does not vary substantially (Figure 2).

#### 4. Conclusions

The impedance and dielectric properties of a solution phase and gel of [BMPyrr][TFSI] were studied in this work, as well as the effect of salt addition.

- The mobility of ions becomes greater when the temperature increases.
- An enhancement of ionic conductivity is observed with an increase of temperature, which could be justified by a reduction of viscosity.
- Conductivity decreases with the addition of salt due to an increase of viscosity, and also decreases with the nanoconfinement of the IL in the matrix scaffolds, probably due to electrostatic interactions between IL and the nano-scaffold.

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