



Recent Advances in Innovative Polymer Electrolytes based on Poly(ionic liquid)s



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ABSTRACT

This article reviews the general strategies for the design of innovative polymer electrolytes using poly(ionic liquid)s. First, we review the properties of poly(ionic liquid)s as solid polymer electrolytes (SPEs). The different factors that affect the bulk ionic conductivity of poly(ionic liquid)s are discussed such as chemical nature of the cation, anion, the spacer, the polymer backbone and its glass transition temperature, the purity and water content. Special attention is given to the optimization of both the ionic monomer chemical structure and macromolecular architecture to achieve the highest possible polymer ionic conductivity ($\approx 10^{-5}$ S/cm at 25 °C). Secondly, the preparation of gel type polymer electrolytes, named “ion gels”, based on ionic liquids and poly(ionic liquid)s is discussed in terms of preparation methods and composition. Due to the presence of free ions, such ion gels provide higher ionic conductivity ($10^{-2} - 10^{-3}$ S/cm at 25 °C) than SPEs. Finally, the actual applications of innovative polymer electrolytes based on poly(ionic liquid)s are summarized and their advantages are discussed.

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1. Introduction

In the last decade, ionic liquids (ILs) have been recognized as key materials for the electrochemical challenges of the present and future. Nowadays, the use of ionic liquids as electrolytes is improving the performance, security, speed, cyclability and long-term stability of various electrochemical devices such as batteries, solar cells, fuel cells, supercapacitors, light-emitting electrochemical cells, actuators, biosensors and field effect transistors among others. However, it is well known that in some devices ionic liquid electrolytes do still present some drawbacks difficult to overcome, such as need of thorough encapsulation due to the leakage of electrolyte. In those cases, solid or quasi-solid electrolytes such as polymer electrolytes have important advantages including mechanical stability, safety and simple processing.

Historically, polymer electrolytes have been classified in two main families. “Solid polymer electrolytes” (SPEs) which are composed of a polymer matrix and a salt. This is the case of the well known combination of poly(ethylene oxide) PEO SPE with a lithium salt. In SPEs the ionic conductivity of the material is associated to both lithium cation and the salt anion which move

through the PEO matrix. The second family of polymer electrolytes is named “gel polymer electrolytes” which are composed of a polymer matrix, a salt and an organic solvent. In the case of gel electrolytes the ionic conductivity is usually higher than in SPEs since the transport of the ions is favored by the presence of the molecular organic solvent. This is exemplified by the generally used in lithium batteries gel electrolytes composed of poly(vinylidene fluoride), a cyclic carbonate solvent and a lithium salt.

Due to the emergence of ionic liquids into the area of polymer electrolytes these definitions needed to be adapted (Fig. 1). Bulk polymeric ionic liquids (PILs) or poly(ionic liquid)s are now considered as solid polymer electrolytes (SPEs). However, differently from conventional SPEs based on poly(ethylene oxide), in the case of poly(ionic liquid)s no additional salt needs to be added to the SPE since the pendant counter-ion is free to move and responsible for the ionic conductivity. Depending on the structure of the backbone of poly(ionic liquid)s, namely polycation or polyanion, the ionic conductivity will be associated with the transport of the counter-anions or counter-cations respectively.

Further on, to increase the conductivity of SPE material another popular strategy consists in the preparation of gel type polymer electrolytes by addition of ionic liquids. This particular type of gel electrolytes where the role of volatile organic solvent is played by nonflammable and nonvolatile ionic liquids is named ion gels. It is

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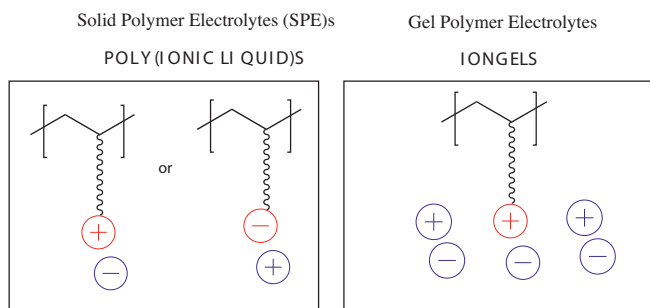


Fig. 1. Graphical representation of SPEs poly(ionic liquid)s and gel type polymer electrolytes named ion gels.

worth to note that ion gels can be prepared using not only poly(ionic liquid)s, but different types of polymeric matrices: non-charged conventional polymers or even siloxane networks made by sol-gel chemistry can be applied as well. Here the ionic conductivity is associated with the transport of the cations and anions of the IL and, in case of poly(ionic liquid)s matrix utilization, cumulatively with the transport of the respective counter-ion.

It is worth to remark the versatility of the polymer electrolyte platform based on poly(ionic liquids), SPEs and ion gels. Since it offers great ability in the designing of cationic and anionic structures and their combinations, one can in principle manipulate properties of material as desired and tune and enhance the ionic conductivity to a very high level (10^{-2} – 10^{-5} S/cm at 25 °C). Furthermore, it allows to selectively choose the type(s) of anion or cation or both which may be responsible of the ionic conductivity of the polymer electrolyte. It is worth to remark that this moving ion plays a pivotal role in any electrochemical device where the ions are inserted into the electrodes during oxidation or reduction reactions. For instance, in the case of cationic poly(ionic liquid) the ionic conductivity will be associated to the counter-anion, such as fluorinated sulfonimides, tetrafluoroborates, cyanamides and so on. Whereas in the case of anionic poly(ionic liquid) the ionic conductivity will be associated only to the counter-cation, which can be inorganic such as Li^+ , Na^+ or organic such as imidazolium, pyrrolidonium or tetraalkylammonium. This produces SPEs with lithium or sodium transfer numbers close to 1 which makes them very interesting SPEs for batteries. However in the case of ion gels the ionic conductivity is associated to both anion(s) and cation(s) of the ionic liquid(s) plus the counter anion(s) of the poly(ionic liquid) matrix.

Altogether, in the last decade there has been an important effort in designing innovative polymer electrolytes both based on single poly(ionic liquid)s and “ion gels”. The goal of this article is to review these developments, to explain what we know so far about the ionic conductivity of these materials and their emerging applications in electrochemical devices. Finally we will give our opinion and an outlook for the future of this vibrating and exciting topic.

2. Design of solid polymer electrolytes (SPEs) based on poly(ionic liquid)s

Although the conductivity and dynamics of polyelectrolytes in solution have been extensively studied for last 80 years [1–3], it

was believed that polyelectrolytes could not play the role of solid ion conductors. Due to extensive ion-pairing only brittle materials with very low bulk conductivity were usually obtained. However, as mentioned in the introduction part, the application of ionic liquid's chemistry to the macromolecular synthesis resulted in the appearance of new intriguing subclass of polyelectrolytes, namely poly(ionic liquid)s. Since poly(ionic liquid)s are composed of ionic species, similar by composition to the structure of commonly used ILs, this allowed to combine all properties of classical polyelectrolytes with those beneficial of ILs, high bulk ionic conductivity, in particular [4–11]. An endless number of possible combinations of anions (BF_4^- , PF_6^- , $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{CN})_2\text{N}^-$, CF_3SO_3^- , etc.) and cations (imidazolium, pyrrolidinium, ammonium, lithium, sodium, etc.), as well as variations in the nature and structure of the main polymer backbone and spacer (Fig. 2), opened broad possibilities for the synthesis of ionic monomers and optimization of the macromolecules architecture with the goal of creating of a polyelectrolyte with enhanced solid state conductivity [8].

The analysis of up to date literature data on poly(ionic liquid)s [8,10–29] allows the establishment of main factors influencing their bulk conductivity, namely: the structure of the cation and anion, the presence, the nature and the length of the spacer, glass transition temperature and molar mass of the studied polymer, the morphology, the purity of poly(ionic liquid) and, finally, the atmosphere's humidity during the conductivity measurements.

2.1. Chemical structure of the cation

The type of cation strongly influences the conductivities of cationic and anionic polymers [18,25,30–33]. Both the nature of heterocycle and its substitutes are playing an important role as it can be tracked on several different series of poly(ionic liquid)s (Fig. 3). Depending on the size of the alkyl spacer, bis(trifluoromethylsulfonyl) imide poly(ionic liquid)s having imidazolium cation covalently attached to the main polymer backbone generally tended to show higher ionic conductivities except for the polymers with 2-substituted imidazolium ring [30,32,33] (Fig. 3a–3b). The subsequent change from the small methyl group [32] as the substitute at the ammonium cation to butyl and finally to the long heptyl one [34] resulted in the improvement of conductivity from 7.4×10^{-10} to $\sim 2.0 \times 10^{-8}$ S/cm at 25 °C (Fig. 3c). The same tendency, i.e. the rise of the conductivity from 7.4×10^{-10} to $\sim 8.5 \times 10^{-7}$ S/cm at 25 °C, was observed for imidazolium bis(trifluoromethylsulfonyl) imide poly(ionic liquid)s with transfer from methyl [32] to butyl [17] group (Fig. 3b and 3c) as the side substitute at the corresponding cation (Fig. 3d). Zhou et al. [34] simultaneously with Gibson et al. [25] have noticed that changing the nature of the substitute in quaternized ammonium or heterocyclic poly(ionic liquid)s from n-alkyl to ethylene oxide containing one leads to enhancement of the ionic conductivity from 3.9×10^{-7} to 1.8×10^{-6} and from 4.5×10^{-9} to $\sim 7.0 \times 10^{-6}$ S/cm at 25 °C, respectively (Fig. 3c and 3e). Another way to influence poly(ionic liquid)'s ionic conductivity is the introduction of the extremely bulky side substitutes that can decrease the packing density of the corresponding polymer and as a result can decrease its T_g . Vygodskii et al. [31,35] have demonstrated that the

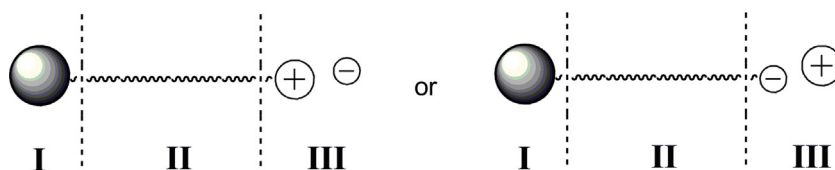


Fig. 2. A schematic representation of ionic liquid like monomer: I – reactive group, II – spacer, III – ion species.

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