



# Polymer effect on lithium ion dynamics in gel polymer electrolytes: Cationic versus acrylate polymer



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## ARTICLE INFO

### Article history:

Received 26 March 2015

Received in revised form 13 May 2015

Accepted 26 May 2015

Available online 11 June 2015

### Keywords:

Polymer electrolytes

ionic liquids

PFG-NMR

conductivity

lithium ion

## ABSTRACT

In this work we study different ternary polymer gel electrolytes in order to analyze the influence of the type of polymer and its concentration on the lithium ion transport. Four ternary systems are prepared, containing either poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)-imide (PDADMATFSI) or poly(methyl methacrylate) (PMMA) as polymeric component, lithium bis(trifluoromethanesulfonyl)-imide (LiTFSI) as conducting salt, and either ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (PYR<sub>14</sub>TFSI) or propylene carbonate (PC) as solvent. We study the lithium ion dynamics in dependence on polymer concentration for all systems. The samples are studied by <sup>7</sup>Li and <sup>19</sup>F Pulsed Field Gradient (PFG) nuclear magnetic resonance (NMR) diffusion experiments of the lithium ion as well as the TFSI<sup>-</sup> anion. The diffusion coefficients of the ions decrease strongly with increasing concentration of PMMA, but they decrease less significantly for increasing concentration of PDADMATFSI. Various comparisons of diffusion coefficient ratios highlight the role of the solvent and the polymer, respectively. Spin-lattice relaxation rates give an insight about the change in short range (local) dynamics of the lithium ion. In summary, the result show that PDADMATFSI acts as an efficient ionic cluster breaker between lithium and TFSI<sup>-</sup> and is thus a far better suitable polymer in electrolytes than PMMA.

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## 1. Introduction

During the last decade a lot of development effort towards new electrolyte materials was focused on liquid electrolytes which combine a very low vapor pressure and a high room temperature ionic conductivity. Ionic liquids, which fulfill the required properties have been more and more intensely studied, since their thermal stability provides an extra advantage over conventional organic solvents [1]. Ionic liquids (ILs) are organic salts with a low melting point (<100 °C) which are widely investigated in different fields of research due to their negligible vapor pressure, high ionic conductivity and wide electrochemical window [2,3]. However, the difficulty using ionic liquids in battery devices is the possibility of leakage, for its liquid nature. The logical choice was to search for highly viscous systems, however maintaining adequate room temperature ionic conductivity for the applications in secondary lithium ion batteries. This led to the development of gels, which essentially consist of liquid electrolyte in a swollen polymer matrix [4–6]. The ionic liquid is doped by lithium salt and dissolved in polymer. Thus, membranes are formed, which show

excellent electrochemical stability, good lithium transport and exceptional mechanical properties [7,8]. However, the addition of polymer generally increases the viscosity substantially, which is accompanied by a considerable decrease in conductivity. For example, Susan et al. [9] investigated polymer gels obtained by polymerization of methyl methacrylate (MMA) in ionic liquid and observed the decrease in conductivity with increasing polymer concentration [9]. Thus, a smart choice of the polymer is required to optimize mechanical stability and conductivity simultaneously. Pont et al. [10] developed a gel system based on a charged polymer. They use the polycation poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)-imide (PDADMATFSI) as polymer in mixtures with PYR<sub>14</sub>TFSI and LiTFSI [10]. The resulting gels show promising properties for use in electrochemical devices and have already been tested for battery application in half cells [11]. In addition, Jeremias et al. [12] demonstrated that the monomeric precursor DADMATFSI is a state of the art ionic liquid and can be successfully polymerized in mixtures with PYR<sub>14</sub>TFSI with high rates of conversion, allowing the in-situ formation of ionogels of desired composition [12]. The transport properties of these gels are influenced by the polymer content, however, the mechanical stabilization by the polymer can be achieved with only minor reduction of the conductivity [12]. Analyzing the local lithium

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dynamics as determined from temperature-dependent spin relaxation rates, it was argued that there are beneficial effects of this particular polymer on  $\text{Li}^+$  mobility, as it reduces the Li-anion coordination [13].

In our present work we compare PDADMATFSI with the above beneficial properties to a classical polymer in electrolytes, PMMA. PMMA has been tested as a neutral,  $\text{Li}^+$ -ion coordinating polymer in electrolytes for  $\text{Li}^+$  ion conduction [14]. This comparison poses the question whether a cationic polymeric ionic liquid (PIL) such as PDADMATFSI, or poly(methyl methacrylate) (PMMA) as an ion-coordinating agent can act more beneficially in polymer electrolyte gels. The aim of this work is to explore any structural advantage of PDADMATFSI in comparison to PMMA concerning its ability to improve the  $\text{Li}^+$  transport.

Efficient  $\text{Li}^+$  transport in ionic liquids is strongly dependent on the degree of dissociation of the Li salt and on the interaction of the lithium ion with the anions of the ionic liquid, as ion pairs or larger clusters might be the dominating species, limiting the  $\text{Li}^+$  contribution to conduction. Complexes of two  $\text{Li}^+$  bridged by three TFSI<sup>-</sup> have been calculated by Borodin et al. [15] and complexes with one  $\text{Li}^+$  and two, three and four TFSI<sup>-</sup> have been concluded from NMR measurements and described by molecular dynamic simulations [15]. Usually the coordination of three to four TFSI<sup>-</sup> with one lithium ion has been experimentally observed and found in simulations [16,17]. Different types of complexes are favored in dependence on the ratio of lithium and anion. The lithium is always coordinated by the sulfonyl oxygen of the anions. In addition larger clusters of different amounts of lithium and TFSI<sup>-</sup> are also possible.

The incorporation of neutral polymer, like PMMA, introduces coordinating oxygen atoms in the system, which can interact with  $\text{Li}^+$  and thus enhance salt dissociation. The strategy is similar to that employed in classical salt-in-polymer electrolytes which employ poly(ethyleneoxide) units in order to coordinate  $\text{Li}^+$  and thus enhance dissociation [18,19]. A disadvantage is, however, the dynamic coupling of the  $\text{Li}^+$  ions to the polymer backbone and the induced dynamic restriction [19]. Therefore, further additives employed are nanoparticles, which can again reduce the lithium coordination to the methacrylate based polymer chains [20,21]. The addition of zwitter-ionic compounds was also tried for an enhancement of salt dissociation to improve conductivity, and in some cases addition of both, zwitter ions and nano-fillers has been tested [22,23]. Unfortunately, in many systems these additives do not have a pronounced effect, or there is even a negative effect on the lithium mobility.

In neutral electrolyte solvents, such as carbonates, optimization of  $\text{Li}^+$  transport focuses on enhancing salt dissociation. PMMA was reported to enhance the dissociation of for example ammonium triflate salt in diethylcarbonate (DEC) [24]. To provide a more efficient lithium transport in relation to that of the anion, i.e. to enhance  $\text{Li}^+$  transference numbers, many different approaches were undertaken, among them restricting the mobility of anions. Saito et al. [25] described the effect of a substituted ionic Lewis acidic group in the polyvinyl butyral (PVB) polymer chain which selectively attracts the anions and restricts their motion [25].

In this work, we compare the two polymers PMMA and PDADMATFSI in polymer electrolyte gels in order to compare the strategy of  $\text{Li}^+$  coordination, which would enhance salt dissociation, but at the cost of reducing  $\text{Li}^+$  mobility, to the strategy of electrostatic attraction of anions to a cationic PIL, which might reduce the cation-anion interaction (see the structures in Fig. 1). Our study is mainly based on determination of diffusivities of the ionic species and systematic comparisons between them. We finally demonstrate an advantage of using a positively charged PIL over the neutral coordinating polymer concerning an improvement of lithium transport.

## 2. Materials and methods

### 2.1. Materials.

The chemicals lithium bis(trifluoromethanesulfonyl)-imide (LiTFSI), poly(methyl methacrylate) (PMMA), poly(diallyldimethylammoniumchloride) (PDADMAC) (20 wt. % aqueous solution, molecular weight 100,000–200,000) and propylene carbonate were purchased from Sigma Aldrich and used without further purification. LiTFSI was dried at 100 °C under ultra-high vacuum ( $\sim 10^{-7}$  bar) for 24 h and then stored inside a glove box under argon atmosphere. The ionic liquid  $\text{PYR}_{14}\text{TFSI}$  was purchased from io-littec (Heilbronn, Germany) with a purity of 99.5%. It was also dried over night at 100 °C under ultra-high vacuum conditions and then stored in a glove box.

### 2.2. PDADMATFSI preparation.

The polymeric ionic liquid, PDADMATFSI, was synthesized by anion exchange from the commercially available PDADMAC following the procedure of Pont et al. [10] to prepare water-free PDADMATFSI. In detail, to prepare PDADMATFSI, 30 mL of 20 wt. % aqueous solution of PDADMAC were added to 100 mL of ultrapure water to dilute the polymer concentration. 300 mL of 100 mM LiTFSI solution was prepared in ultrapure water. At room temperature the LiTFSI solution was added drop wise to the PDADMAC solution and stirred. After 4 hours of stirring it was filtered and a white precipitate was separated, to which 100 mL of 150 mM LiTFSI solution was added, stirred and filtered. This process was repeated for 3 times consecutively to effectively remove remaining chloride ions from the precipitate. The presence of remaining chloride ions in PDADMATFSI was tested by addition of  $\text{AgNO}_3$  solution to the concentrated polymer solution, where no white precipitate and no turbidity of the polymer solution was observed. Finally, the precipitate was washed several times in ultrapure water and dried first at 50 °C for 24 h in a vacuum oven, subsequently dried at 90 °C under ultrahigh vacuum for 24 h, and finally stored in a glove box under argon atmosphere.

**Table 1**

Compositions of the four series of polymer electrolyte gels prepared either with PMMA or PDADMATFSI in PC or IL, respectively.

| PYR <sub>14</sub> TFSI(mL):<br>PMMA(mg): LiTFSI(mg) | PYR <sub>14</sub> TFSI(mL):<br>PDADMATFSI(mg):LiTFSI(mg) | PC(mL):<br>PMMA(mg): LiTFSI(mg) | PC(mL):<br>PDADMATFSI(mg): LiTFSI(mg) |
|---|--|---------------------------------|---------------------------------------|
| 2: 0: 287   | 2: 0: 287  | 2: 0: 287                       | 2: 0: 287                             |
| 2: 100: 287   | 2: 406: 287  | 2: 100: 287                     | 2: 406: 287                           |
| 2: 150: 287   | 2: 507.5: 287  | 2: 150: 287                     | 2: 507.5: 287                         |
| 2: 200: 287   | 2: 609: 287  | 2: 200: 287                     | 2: 609: 287                           |
| 2: 250: 287   | 2: 710.5: 287  | 2: 250: 287                     | 2: 710.5: 287                         |
| 2: 300: 287   | 2: 812: 287  | 2: 300: 287                     | 2: 812: 287                           |
| –   | –  | 2: 400: 287                     | –                                     |

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