

# Influence of anion structure on ion dynamics in polymer gel electrolytes composed of poly(ionic liquid), ionic liquid and Li salt



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## ABSTRACT

To investigate the influence of anion structure on physical properties of electrolytes we used five different anions, namely (FSO<sub>2</sub>)<sub>2</sub>N (FSI, FSA), (CN)<sub>2</sub>N (DCA), (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N (TFSI, TFSA), CF<sub>3</sub>SO<sub>3</sub> (TfO) and (CF<sub>3</sub>SO<sub>2</sub>)N(CN) (TFSAM), and investigated them in a series of polyelectrolytes, ionic liquid (IL)/Li salt mixtures and in ternary ion gels (poly(ionic liquid)/ionic liquid/Li salt), respectively. Both the poly(ionic liquid) (PIL) poly(diallyldimethylammonium) (PDADMA) and the ILs employed in the study have the same pyrrolidinium anion. To isolate solely the effect of the anion a common chloride precursor PIL was used to maintain constant the average degree of polymerization ( $DP_n$ ) and chain dispersity. The systems were analyzed in terms of ionic conductivity, electrochemical stability vs Li<sup>+</sup>/Li, ion diffusion (multinuclear Pulsed Field Gradient NMR) and local lithium ion dynamics (<sup>7</sup>Li spin lattice relaxation rates). Concerning optimization of any of these parameters, different orders of the anion series are obtained and discussed in terms of structural aspects and ion coordination. In particular, the coordination strength of the –CN group to the lithium ion is higher than the coordination strength of the oxygens of the –SO<sub>2</sub>CF<sub>3</sub> fragment. As a result the lithium ion in the TFSAM samples is primarily coordinated by the –CN group. Detailed structure/property relationship analysis demonstrated that for those applications of ion gels (capacitors, sensors, etc.) where a high conductivity is a primary demand, while the electrochemical stability is not essential, the FSI anion will be the best choice. However, for energy storage systems such as Li metal batteries preferably TFSI but also TFSAM anions will represent the best compromise of relevant parameters.

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## 1. Introduction

During the last decade the need for safe and efficient energy storage devices is rapidly expanding [1]. The commonly known lithium-ion-battery technology, using organic polar solvent/Li salt electrolytes, has still some drawbacks like the flammability and the leakage of the liquid electrolyte [2]. To overcome the problem of organic solvents, the ionic liquids (ILs), representing salts with a melting point below 100 °C, are widely investigated due to their

negligible vapor pressure, nonflammability, high ionic conductivity and the wide electrochemical stability window [3,4]. However, as leakage of the ionic liquid electrolyte is still possible, the research efforts further focused on their stabilization by various polymer matrices, thus combining the advantages of ILs with those of polymers and producing the so-called “ion gels”, consisting of a polymer, IL and a lithium salt [5,6]. The ion gels can be prepared by mixing of ILs or ILs/Li salts with non-charged conventional polymers such as polyethylene oxide (PEO) [7] or with a poly(ionic liquid) (PIL) [6,8,9]. The advantages of the latter in comparison to a neutral polymer matrix consist in less amount of IL needed for reaching high levels of ionic conductivity (45–60 wt% of IL for 10<sup>−4</sup> S/cm at 25 °C [10,11] and in higher affinity of

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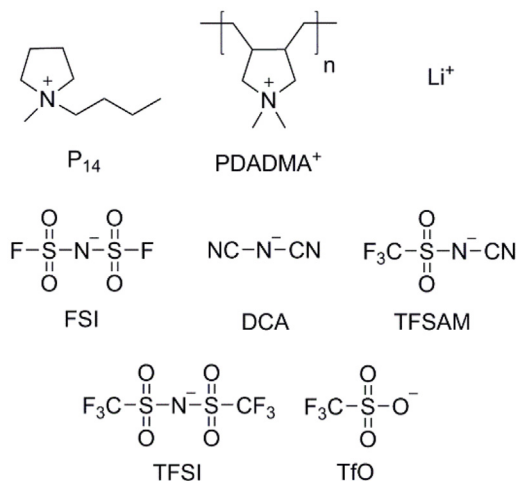
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ILs to charged macromolecules due to the electrostatic interactions [12] and as a result in better compatibility and non-leakage even under pressure/vacuum impact.

Poly(diallyldimethylammonium) bis(trifluoromethylsulfonyl) imide (PDADMA TFSI, correct IUPAC name PDADMA TFSA) can be considered as one of the most popular PILs for the preparation of ion gels because of the commercial availability of the starting chloride polyelectrolyte with different molar masses [6]. For example, Pont et al. synthesized and studied ion gels based on PDADMA TFSI, *N*-butyl-*N*-methylpyrrolidinium TFSI (Pyr<sub>14</sub>TFSI) and LiTFSI [13]. Furthermore, the same ion gel was successfully applied as efficient separator in Li batteries working at 40 °C [11]. Jeremias et al. could show that the monomeric form diallyldimethylammonium TFSI (DADMA TFSI) is an ionic liquid with state-of-the-art properties for ion transport [14]. In mixtures with an inert IL and a Li salt, a polymer gel electrolyte can be formed by simple UV-curing of DADMA TFSI [14]. Furthermore, varying the composition of ion gels Bhandary et al. have demonstrated that PDADMA TFSI applied as a host matrix for ternary electrolytes has beneficial electrostatic interactions, which (i) enhance the Li ion mobility and conductivity of the system in comparison to an uncharged polymer network [15] and enhance the local Li ion dynamics [12].

In order to improve the ion mobility and the conductivity in ILs, and in respective ion gels, attempts were made to introduce new anions. Thus, in 2001 MacFarlane et al. reported that the small and delocalized dicyanamide ((CN)<sub>2</sub>N, DCA) anion forms room temperature ILs with asymmetric and cyclic aliphatic quaternary ammoniums [16]. Further on, Ignatiev introduced cyano groups into the borate anion, thus forming tetracyanoborate bearing organic salts to substitute the tetrafluoroborate ones. An approach to reduce the size of the anion with the preservation of its high charge delocalization was followed during the preparation of room temperature ILs with bis(fluorosulfonyl)imide (FSI) anion [17]. Another trend to decrease melting points and viscosities of ILs consisted in the introduction of asymmetry in the anion's structure and resulted in appearance of salts with 2,2,2-trifluoro-*N*-(trifluoromethylsulfonyl) acetamide (CF<sub>3</sub>SO<sub>2</sub>-N-COCF<sub>3</sub>, TSAC) [18], 2,2,2-trifluoromethylsulfonyl-*N*-cyanoamide (CF<sub>3</sub>SO<sub>2</sub>-N-CN, TFSAM) [19], fluorosulfonyl-*N*-(trifluoromethylsulfonyl)imide (CF<sub>3</sub>SO<sub>2</sub>-N-SO<sub>2</sub>F, FTI [20]) and trifluoromethylsulfonyl-*N*-(nonafluorobutylsulfonyl)imide (CF<sub>3</sub>SO<sub>2</sub>-N-SO<sub>2</sub>C<sub>4</sub>F<sub>9</sub>) [21] anions. At this, TSAC, TFSAM and FTI can form ILs even with the symmetrical tetraethylammonium cation and show higher conductivities than that of organic salts bearing the most popular TFSI anion.

Recently it was revealed that the basic rules governing the ionic conductivity in ILs are not always applicable to PILs [6,22]. For example, while the DCA anion imparts one of the highest known conductivities to ILs, its application in polymers did not lead to optimal results [22]. The transfer from pure ILs to ion gels, representing a complex system, can completely change the known dependencies and is rather poorly studied. Therefore, to explore the influence of an anion structure on physical properties of ternary ion gels (IL/PIL/Li salt), in particular on their transport properties, a series of ionic liquids with Pyr<sub>14</sub> cation, PDADMA based PILs and lithium salts bearing five different anions was prepared (Scheme 1). To isolate the effect of the anion on physical properties of ion gels, a common chloride precursor PIL was used to maintain constant the average degree of polymerization ( $DP_n$ ) and chain dispersity. The long range ion dynamics in IL/PIL/Li salt materials was analyzed by multinuclear Pulsed Field Gradient NMR measurements (PFG-NMR) of the diffusion coefficients. In addition, the local lithium environment and ion dynamics were characterized by spin lattice NMR relaxation measurements ( $T_1$ ) of <sup>7</sup>Li. Furthermore, the conductivity obtained by impedance spectroscopy and the electrochemical stability obtained by cyclic



Scheme 1. Components of the binary and gel electrolyte systems.

voltammetry were thoroughly investigated and are discussed in detail.

## 2. Experimental

### 2.1. Materials

*tert*-Butanol (99.5%, extra pure, Acros), cyanogen bromide solution (5.0 M in acetonitrile, Aldrich), lithium bromide (99+ %, Acros), silver nitrate (AgNO<sub>3</sub>, ≥ 99.0%, Fluka), silver trifluoromethanesulfonate (AgTfO, ≥ 99 %, Aldrich), sodium dicyanamide (NaDCA, 97%, Acros), potassium bis(fluorosulfonyl)imide (KFSI, 99%, Solvionic), lithium tetrafluoroborate (LiBF<sub>4</sub>, 98%, Aldrich) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP, ≥ 99 %, Aldrich) were used without further purification. Reagent-grade dichloromethane, acetonitrile, hexane, ethyl acetate and diethyl ether were obtained from Aldrich or Merck and were dried by vacuum distillation over P<sub>2</sub>O<sub>5</sub>. *N*-Methylpyrrolidine (98%, Acros) and 1-bromobutane (99%, Acros) were distilled under inert atmosphere over CaH<sub>2</sub>. Trifluoromethanesulfonamide (97%, ABCR) and potassium *tert*-butoxide (Acros, 98%) were sublimed in high vacuum (< 1 mm Hg) at 75–80 and 200–210 °C, respectively. Potassium 2,2,2-trifluoromethylsulfonyl-*N*-cyanoamide (KTFSAM) was synthesized according to the procedure described previously [19]. Poly(diallyldimethylammonium) chloride (PDADMA Cl,  $M_w = 181000$  g/mol,  $M_w/M_n = 2.02$ ,  $[\eta]_{1\text{Maq,NaCl}} = 0.67$  dL/g (30 °C)) was provided by Prof. C. Wandrey (Ecole Polytechnique Fédérale de Lausanne (EPFL)).

### 2.2. Li salts

Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI, ≥ 99 %, Aldrich), lithium trifluoromethanesulfonate (LiTfO, ≥ 99 %, Aldrich) and the Li salts synthesized in this work were dried for 24 h at 100 °C/10<sup>-7</sup> bar prior their utilization.

For synthesis of LiDCA, AgNO<sub>3</sub> (15.31 g, 0.090 mol) was dissolved in 50 mL of distilled water and added dropwise to the solution of NaDCA (8.69 g, 0.095 mol) in 50 mL of H<sub>2</sub>O at ambient temperature. The stirring was continued for 1 h, whereupon the obtained white precipitate was filtered off and thoroughly washed with distilled water. The AgN(CN)<sub>2</sub> was quantitatively collected from the filter and suspended in 60 mL of water. To the obtained suspension the 25 mL of aqueous solution of lithium bromide (6.52 g, 0.075 mol) was added dropwise upon stirring and the formation of a yellow precipitate was observed. The suspension

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