7Li nuclear magnetic resonance studies of dynamics in a ternary gel polymer electrolyte based on polymeric ionic liquids

CrossMark

Martin Gouverneur [2], Sebastian Jeremias [1], Monika Schönhoff *

Institute of Physical Chemistry, University of Muenster, Corrensstraße 28/30, 48419 Münster, Germany

ABSTRACT

The influence of the polymeric ionic liquid (PIL) Poly(diallyldimethylammonium bis(trifluoromethyl-sulfonyl) imide) (PDADMATFSI) on the lithium dynamics was investigated in a ternary gel polymer electrolyte consisting of PDADMATFSI as stabilizing polymer, ionic liquid (1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide, P_{14}TFSI) and lithium salt (lithium bis(trifluoromethylsulfonyl) imide, LiTFSI). The diffusion coefficient of the lithium ions is investigated by pulsed-field-gradient NMR, the conductivity of the electrolyte is determined by impedance spectroscopy. The local lithium dynamics is characterized by 7Li spin lattice relaxation rates (R_1). The relaxation rates are well described by Blombergen-Purcell-Pound (BPP) theory at all polymer concentrations (up to 45 mol%), implying that the Li dynamics is governed by one single motional mode. Interestingly, activation energies for this motion decrease from 20 kJ/mol to 15 kJ/mol with increasing polymer content and are independent on the salt content. We thus conclude that the polymer is interacting with the anion coordination shell, which is accompanied by a very beneficial effect on the local lithium dynamics, as the polymer PDADMATFSI reduces the Li-TFSI interactions. This result is promising for further investigations for potential use of PDADMATFSI-containing gels as electrolytes in energy storage devices.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

For the development of renewable energies, electric cars and mobile applications the improvement of energy storage devices has become very important in the last years [1]. The state of the art technology, the Lithium-ion-battery, has despite of its high capacity still drawbacks like leakage and flammability of the typically used electrolytes [2]. To overcome these problems, polymer electrolytes, most of them PEO-based salt-in-polymer electrolytes, have been investigated over the last decades. However, most of these systems do not have a sufficient conductivity ($>10^{-3}$ S/cm) at room temperature [3–5]. To improve the conductivity of the polymer based systems, gel polymer electrolytes have been introduced due to their higher conductivity and mechanical stability [6–8]. Another approach is the use of ionic liquids (IL) as electrolytes because of their unique properties like

no flammability and high ion conductivity [9–12]. To combine the advantages of the gel electrolytes with those of IL, they are used as solvents for polymers [13–15]. Especially the use of polymerized ionic liquids (PIL) has become popular due to their benefits in tuneable solubility, electrochemical stability and ionic conductivity [16–18]. Pont et al. first reported about the synthesis of PDADMATFSI, conductivity and electrochemical stability measurements in combination with 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide (P_{14}TFSI) and lithium bis(trifluoromethylsulfonyl) imide (LiTFSI). They could achieve conductivities about 10^{-4} S/cm at room temperature and an electrochemical stability window over 6.0 V [19]. Appetecchi et al. investigated a ternary electrolyte based on PDADMATFSI in a Li/LiFePO$_4$ solid state cell [20]. We have recently shown that the monomeric form, diallyldimethylammonium bis(trifluoromethylsulfonyl) imide (DADMATFSI), is an IL with similar properties in conductivity and diffusion as the state of the art IL P_{14}TFSI, while in addition it can be polymerized into PDADMATFSI. Polymerization can be performed in-situ in binary mixtures of IL, yielding the desired polymer content in the gel and binary mixtures of PDADMATFSI/ P_{14}TFSI show conductivities around 10^{-3} S/cm at 25 °C [21].

In spite of the promising results described above for gel-polymer electrolytes based on PDADMATFSI the molecular interactions and dynamics and the mechanisms leading to such

* Corresponding author. +49 251 8323419.
E-mail addresses: m_gouv01@uni-muenster.de (M. Gouverneur), s_jere01@uni-muenster.de (S. Jeremias), schoenho@uni-muenster.de (M. Schönhoff).
[1] Present address: MEET, University of Muenster, Corrensstraße 46, 48149 Münster, Germany. Tel.: +49 251 83 36757.
[2] Tel.: +49 251 8323415.

outstanding transport properties have not yet been considered. The interaction between the polymer-solvent mixture and the lithium ions is the most important criterion for the lithium ion conductivity. These interactions are not well understood in these systems, because only total conductivities have been determined so far. Instead, the charge transport and the lithium dynamics in the gel electrolyte have to be evaluated. This work is therefore focused on the long range and local mobility of the lithium ions in combination with PDADMATFSI. One of the key questions in this work is the influence of the polymer concentration on the lithium dynamics. Hence the measurements are carried out at different polymer concentrations and temperatures. The self-diffusion coefficient of the lithium ions is investigated via pulsed-field-gradient NMR (PFG-NMR), which gives information about the long range transport [22]. Furthermore, the overall conductivity is determined by impedance spectroscopy [23]. To get more information about the influence of the polymer on the local ionic mobility, especially the microscopic lithium motion, ^{7}Li spin-lattice relaxation measurements are carried out [24,25]. These measurements are important for understanding the transport processes and the local coordination of the lithium ions in this new type of polymer electrolyte. The results show a unique novel effect, which is that the cationic PDADMA partly compensates the reduction of the Li$^+$ dynamics, which is induced by the viscosity enhancement upon polymer addition: This effect comes about by the polymers preferential association with the anions, reducing their coupling to the Li$^+$ ions and thus yielding higher Li$^+$ mobilities in comparison to that of the anions. Thus, the results promote cationic PIL as outstanding materials in Li conducting gel electrolytes.

2. Experimental

2.1. Materials

The IL 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (P$_{14}$TFSI, 98,5%, Fluka Analytical) and the salt lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, 99%, Sigma Aldrich) were used without further purification. Both were dried at 100 °C at 10^{-7} bar for 24 hours. The polymer poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl) imide (PDADMATFSI) was synthesized from poly(diallyldimethylammonium) chloride (PDADMAC, 20wt%, M$_w$ = (100,000 to 200,000) g/mol, Sigma Aldrich) and LiTFSI via anion exchange. 0.23 M PDADMAC solution and 0.1 M LiTFSI solution in water were mixed and stirred for 4 hours. After washing with water, the water-insoluble precipitate was mixed with 0.1 M LiTFSI solution again. The washing of the

precipitation and mixing with LiTFSI solution was repeated three times to complete the anion exchange. The polymer was freeze-dried for one week and dried in the oven at 100 °C in vacuum for 48 hours. The components of the gel electrolyte are displayed in Scheme 1.

P$_{14}$TFSI was used as a solvent for the polymer and the lithium salt. These components were added into the IL in defined molar ratios together with 2 mL acetone as solvent and mixed by stirring for 24 h. After stirring the acetone was evaporated at 40 °C and atmospheric pressure and the sample was dried at 100 °C for 48 h in vacuum again. The notation of the molar ratios is done in the following way: IL: polymer: lithium salt. Thus, for example 20:02:02, means 20 mol of IL mixed with 2 mol of polymer (monomer concentration) and 2 mol of Li salt. Two series of samples with different salt content were prepared, i.e. 20:X:02 and 20:X:04. The salt concentration is 0.3 mol/L and 0.6 mol/L LiTFSI, respectively, when only the IL is considered as solvent and the volume of the polymer is neglected.

2.2. NMR Experiments

For all NMR measurements a Bruker 400 MHz Avance NMR spectrometer with a gradient probe head (Bruker, Diff30) with a selective high temperature rf-insert (for 5 mm NMR tubes) for ^{7}Li nuclei and a maximum gradient strength of 11.8 T m^{-1} was used. The temperature control was performed using a GMH 3710 controller with a PT100 thermocouple (Greisinger electronics, Germany). ^{7}Li spectra of all compositions showed a single spectral line with an FWHM in the range of 20 to 200 Hz (see examples in supporting information, part B), and showed no indication of additional, broader spectral components.

The spin-lattice relaxation time T_1 was measured in the same probe head with the Inversion Recovery pulse sequence, π-τ-$\pi/2$-acquisition [26].

$$M_z = M_0 \left[1 - 2\exp\left(-\frac{\tau}{T_1}\right) \right] \qquad (1)$$

The recovery curve was fitted by Eq. (1) to extract the spin-lattice relaxation time T_1. The $\pi/2$-pulse length was 8 µs for ^{7}Li. The measurements were carried out in a temperature range of 20 °C to 150 °C. The observed T_1 times were in the range of 300 to 700 ms, T_2^* was about 50 ms. The relaxation delay d1 was set to 5 s, the delay τ was varied in the range of 0.02 s to 5 s. Examples for the evaluation of T_1 from intensity raw data can be found in the supporting information, part D.

The self-diffusion coefficient of the lithium ions (^{7}Li) was measured using pulsed-field-gradient NMR (PFG-NMR) [22,27].
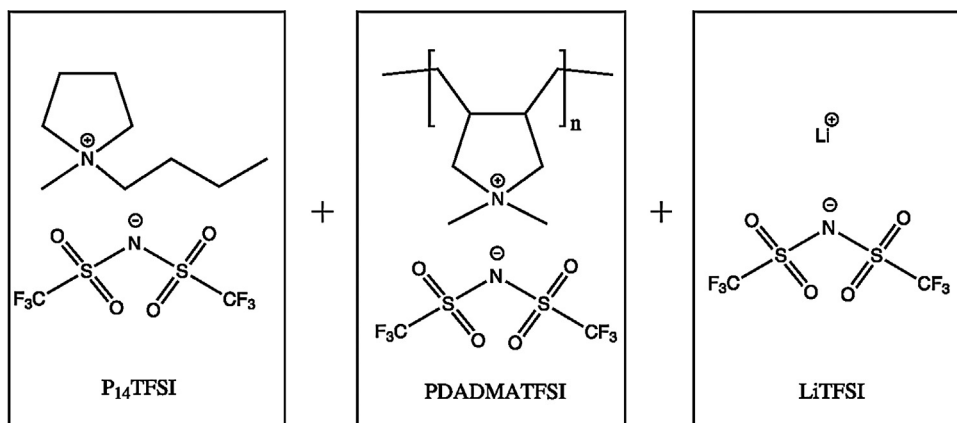
Scheme 1. Components of the gel electrolyte, left: IL P$_{14}$TFSI, middle: PIL PDADMATFSI, right: Lithium salt LiTFSId.