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Ion conduction of branched polyethyleneimine–lithium bis(trifluoromethylsulfonyl) imide electrolytes

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ABSTRACT

Ionic conductivity of polymer electrolytes containing branched poly (ethylene imine) (BPEI) and lithium bis(trifluoromethyl sulfonyl)imide (LiTFSI) was measured between temperatures of 20 and 70 °C and molar ratios of 20:1 and 400:1. The electrolytes were characterized by impedance spectroscopy, differential scanning calorimetry, and viscosity measurements. At room temperature, the maximum conductivity was 2×10^{-6} S/cm at a molar ratio of 50:1. The molar conductivity of the electrolytes displayed first a minimum and then a maximum upon increasing salt concentration. A proportionality of molar conductivity to segmental mobility was seen from glass transition temperature and viscosity measurements. Analysis of the Walden product and isoviscosity conductivity showed that the percentage of ions bound in ion pairs increased at low concentrations below 0.1 mol/kg. The average dipole moment decreased with salt concentration. The temperature dependence of the ionic conductivity showed an Arrhenius behavior.

1. Introduction

New and improved technologies are under intense worldwide development for renewable energy and for energy efficiency. The importance of ion conductors (electrolytes) is well established for a number of these technologies [1,2]. One of the key energy saving technologies - which is of particular relevance for the present work – employs electrochromic "smart" windows, in which electrolytes are used as ion conducting layers joining two different electrochromic thin films [3–5]. Polymer electrolytes, comprising macromolecular species with dissolved salts, may be more convenient than other types of electrolytes for electrochromic applications and allow facile fabrication of devices for large-area applications [6].

Polymer electrolytes based on poly (ethylene oxide) (PEO) have been thoroughly studied for electrochromic applications [7–10]. However, its nitrogen analogue, i.e., linear poly (ethylene imine) (LPEI), may be more suitable than PEO to form complexes with salts, which is a consequence of nitrogen being a better donor atom than oxygen [11]. Even more favorable properties can be found for branched PEI (BPEI), whose ability to make homogeneous amorphous salt complexes at low salt concentrations makes it superior to the linear variety [12]. Based on considerations of this kind, we have recently focused on polymer electrolytes containing BPEI and lithium bis(trifluoromethyl sulfonyl)imide (LiTFSI), and we have reported results from differential scanning calorimetry (DSC) and viscosity measurements [13], and on mechanisms for ionic relaxation [14]. In the present paper, we take the next step in our investigation and consider ion conduction, in particular effects of ion association and mobility.

Some studies on PEI-based polymer electrolytes have been done before. Thus DSC and conductivity measurements have been carried out on polymer electrolytes prepared from low-molecular-weight LPEI and various Li salts such as LiF, LiCl, LiBr, LiI, LiSCN, $LiClO_4$ and $LiBF_4$, and a room temperature conductivity of about 1×10^{-8} S/cm has been observed [15]. Complex formations of PEI with sodium triflate and conductivity behaviors of the complexes have been studied and a nearly linear Arrhenius type behavior has been obtained [16]. In addition, salt concentration and temperature dependence of the conductivity of BPEI with lithium triflate have been investigated [17]. Polymer electrolyte formation of LPEI and poly (N-methylethyle imine) (PMEI) with various lithium salts has been studied, and it was found that PEI systems are more conductive than PMEI when the salt concentration was low [18].

When a salt is dissolved in a polymer, there can in principle be present free ions, ion pairs and triple ions, as well as higher aggregates, and all of these can influence the conduction in the electrolyte [19]. Free ions contribute directly to the conductivity, but ions can also link to the polymer and become inactive. Furthermore, free ions and/or triple ions can interact with polymer chains and form transient cross-links [20], which decrease the chains' segmental flexibility. Hence, the segmental motion of the polymer

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chains is usually determining the rate of ion transport [20]. Ion pairs can also be formed; they do not contribute to the charge transfer and the ion conductivity of the polymer electrolyte. Effects of ion pairing and mobility contribute to a characteristic behavior of the molar conductivity as seen for many polymer electrolytes [20]. Clearly, there are numerous effects influencing the electrolyte conduction, and the purpose of this paper is to elucidate the ionic conductivity mechanisms for BPEI–LiTFSI electrolytes with different salt concentrations.

2. Experimental

2.1. Materials

BPEI with an average molecular weight of 10,000 (purity 99%) was supplied by Alfa-Aesar. The Li salt LiTFSI ($LiN(CF_3SO_2)_2$, 99.95%) and anhydrous methanol (CH_3OH, 99.8%) were obtained from Sigma–Aldrich and Merck, respectively. BPEI was dried before use at 65 °C and 10^{-1} mbar for 48 h. LiTFSI was used after drying at 140 °C and 10^{-1} mbar for 72 h. Methanol was used as received. All materials were stored under dry (<1 ppm H_2O) conditions in a glove box containing argon.

2.2. Sample preparation

In order to form the polymer electrolyte, LiTFSI was first added to the methanol and was stirred. After the salt dissolved in methanol, BPEI was added to the homogeneous solution. Finally, BPEI–LiTFSI complexes were obtained in adhesive and transparent form by removing methanol at 65 °C and 10^{-1} mbar for 48 h. The water content in the samples was found to be below 0.5%, as determined by measuring the relative weight change of the polymer electrolytes on a TGA Q500 thermo-gravimetric analyzer.

BPEI–LiTFSI electrolytes were prepared at values of the molar ratio [N]:[Li], being 400:1, 200:1, 100:1, 50:1, and 20:1. The [N]:[Li] ratio was calculated by dividing the number of moles of BPEI repeated units to the number of moles of LiTFSI. The salt concentration of the electrolytes (c) was obtained as the number of the moles of solute (LiTFSI) per total mass of the solution (BPEI–LiTFSI) in units of mol/kg. The density, ρ, was obtained by dividing the total mass of the electrolyte, obtained from weighing, by the measured volume. The molar concentration of the electrolytes can be obtained by multiplying the salt concentration and the density of the electrolytes. The conversion of molar ratios to the salt concentration and the density of the electrolytes is given in Table 1.

2.3. Characterization techniques

Conductivity measurements were performed on a Novocontrol BDC-N dielectric interface together with a Solartron 1260 frequency response analyzer in the frequency range 10^{-2}–10^{7} Hz. The applied AC voltage was chosen as 1 V in order to avoid noise in the high frequency range. The sample cell consisted of two parallel stainless steel electrodes, with diameters of 20 mm, separated by a ring-shaped Teflon spacer with 1 mm thickness and 3.1 mm height. The temperature was kept constant during each measurement with an accuracy of 0.5 °C. All impedance measurements were done inside a glove box under argon atmosphere to avoid the influence of humidity on the conductivity.

Table 1
Molar ratio, salt concentration c, and density of PEI–LiTFSI electrolytes.

[N]:[Li]	c (mol kg^{-1})	Density (kg dm^{-3})
400	0.06	1.10
200	0.11	1.07
100	0.22	0.93
50	0.41	0.86
20	0.87	0.78

The ionic conductivity was obtained from the ionic resistance via the equation:

$$\sigma = \frac{1}{R}\frac{d}{A}, \tag{1}$$

where R is the ionic resistance of the electrolyte, d is the thickness of the electrolyte, and A is the area of the electrolyte in contact with the electrode surface.

DSC measurements were done on a TA Instruments Q1000 instrument between −80 and +80 °C with a temperature precision of 0.05 °C. The electrolytes were first heated, then cooled, and finally heated again with heating and cooling rates of 10 and 5 °C/min, respectively.

Viscosity measurements were performed on a Brookfield DV-II + Pro viscometer with a viscosity accuracy of ±1.0% at temperatures between 25 and 85 °C.

3. Results

Ionic conductivity measurements were done for different molar ratios of the BPEI–LiTFSI electrolytes between the temperatures 20 and 70 °C. At room temperature, the maximum conductivity was 2×10^{-6} S/cm at a molar ratio of 50:1.

The ionic conductivity of polymer electrolytes can be written as [21]:

$$\sigma = nq\mu, \tag{2}$$

where, n is the volume concentration of (free) charge carriers, q is the charge, $\mu = qD/kT$ is the average ionic mobility of cations and anions, D is the average diffusion constant, k is Boltzmann's constant and T is temperature. According to this relation, ionic conductivity is proportional to the concentration of free ions and the mobility of the ions. It is useful to plot the molar conductivity (Λ), which was obtained by dividing the ionic conductivity by the salt concentration according to [22]:

$$\Lambda = \frac{\sigma}{c}. \tag{3}$$

Fig. 1 shows the concentration dependence of the molar conductivity at temperatures between 20 and 70 °C for BPEI–LiTFSI electrolytes. With increasing salt concentration, one observes first a minimum and then a maximum in Λ. This behavior is typical for the

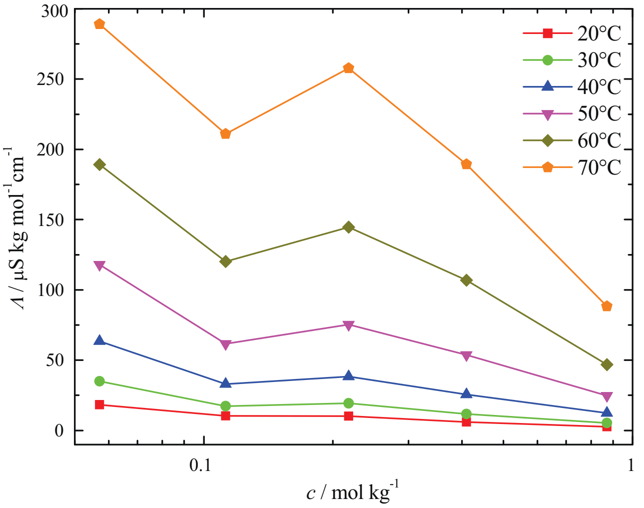

Fig. 1. Molar conductivity Λ *versus* salt concentration c of BPEI–LiTFSI at the shown temperatures.