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Effect of molecular weight on conductivity of polymer electrolytes

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ABSTRACT

The ionic conductivity, σ, of mixtures of poly(ethylene oxide) (PEO) and lithium bis(trifluoromethanesulfone) imide (LiTFSI) was measured as a function of molecular weight of the PEO chains, M, over the range 0.2–5000 kg/mol. Our data are consistent with an expression $\sigma=\sigma_0+K/M$ proposed by Shi and Vincent [Solid State Ionics 60 (1993)] where σ_0 and K are exponential and linear functions of inverse temperature respectively. Explicit expressions for σ_0 and K are provided.

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1. Introduction

Solid polymer electrolytes remain the subject of continual interest in the scientific community for their potential use in high specific energy, solid state batteries [1]. These materials are formed by the complexation of a low lattice-energy salt with solvating polymers [2,3]. Poly(ethylene oxide) (PEO) has been the most widely studied solvating polymer due to its ability to solvate a wide variety of salts through interaction of its ether oxygens with cations.

It is widely believed that ion conduction in an amorphous homopolymer above the glass transition temperature takes place through two mechanisms [4,5]. The first mechanism is a result of the segmental motion of the chains surrounding the salt ions, creating a liquid-like environment around the ion. Ions migrate by hopping between adjacent liquid-like environments. This mechanism is dependent on labile interactions between the ion and the polymer chain, and is thus affected by chemical composition of the polymer and temperature. It is, however, independent of the molecular weight of the chain. The second mechanism of ion conduction is attributed to diffusion of the entire polymer chain with coordinated ions. This mechanism is similar to diffusion of salts in traditional low molecular weight electrolytes such as water and alkyl carbonates wherein ions diffuse with "shells" of coordinated solvent molecules. Since polymer diffusion coefficients decrease rapidly with increasing molecular weight [6–8] the second mechanism is only applicable in low molecular weight polymers. A thorough study of these mechanisms requires studies of ion transport as a function of chain length over a wide range of molecular weights. Further, these studies should be conducted on nearly monodisperse model polymers synthesized by techniques such as anionic polymerization. In simple amorphous polymer melts, it has been shown that the motion of long chains in the presence of a small concentration of short chains is profoundly different from that in their absence due to entanglement dynamics [9,10]. Upon the addition of salt to the system, such entanglement dynamics are coupled to the formation of dynamic cross-links between the salt and the polymer [11].

The effect of polymer molecular weight on transport in polymer electrolytes has, to our knowledge, only been addressed in three prior studies. In a pioneering publication, Shi and Vincent [12] determined the lithium cation diffusion coefficient, D_{Li}, as well as steady state current, I_s^+, of mixtures of lithium triflate and PEO as a function of the PEO molecular weight, M. Pulsed field gradient (PFG) nuclear magnetic resonance (NMR) was used to measure D_{Li} while DC measurements on the polymer/salt mixtures sandwiched between two lithium foils were used to measure I_s^+. They proposed equations for the transport coefficients based on theories of polymer dynamics such as the Rouse model for diffusion of short chains and the reptation model for the diffusion of long chains. In a subsequent publication, Hayamizu et al. [13] determined D_{Li} and ionic conductivity, σ, in mixtures of lithium bis(trifluoromethanesulfone)imide (LiTFSI) and PEO as a function of M. Impedance spectroscopy was used to measure σ. More recently, Diddens et al. [14] used molecular dynamics simulations to determine D_{Li} in PEO/LiTFSI mixtures as a function of M. They demonstrated excellent agreement between simulation results [14] and experiments [13].

The goal of this paper is to augment the existing experimental data on the effect of M on σ in PEO/LiTFSI mixtures. In previous studies, our group has reported on the molecular weight dependence of conductivity and salt diffusion coefficient in PEO-based block copolymer

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electrolytes over a wide range of molecular weights [15–17]. The data presented here provide a baseline for analyzing the effect of polymer molecular weight on ion transport in these more complex systems.

2. Experimental

2.1. Polymer electrolyte preparation

Poly(ethylene oxide) samples were obtained from Polymer Source, Inc. The polymers used in this study can be found in Table 1 and are labeled PEO(x), where x indicates the number averaged molecular weights of the samples in kg/mol. A high molecular weight PEO sample which we label PEO(5000) was obtained from Aldrich. The polydispersity index of this sample was not provided but we expect it to be significantly higher than 1.15. PEO(5000) was dissolved in acetone and recrystallized. The other polymers were used as received. Argon gloveboxes (MBraun and Vacuum Atmospheres Company) with oxygen and water at sub-ppm levels were used for all sample preparation and testing steps. All polymers were dried at 100 °C under vacuum in a glovebox antechamber for at least 24 h, except PEO(0.2) which was received in an ampule under argon, opened in the glovebox, and used as received. LiTFSI salt, obtained from Novolyte, was transferred from its air-free packaging into a vial inside of a glovebox, and then dried at 120 °C under vacuum in a glovebox antechamber for three days.

LiTFSI salt was added directly to PEO(0.2) and PEO(0.6) and stirred at 90 °C for about 12 h. The rest of the electrolyte samples were prepared by blending a PEO/benzene solution with the necessary amount of a 25 wt % solution of LiTFSI salt in tetrahydrofuran (THF). Benzene and THF were purified using an MBraun solvent purification system to remove water and other impurities. For PEO(10), PEO(20), PEO(50), PEO(360), and PEO(5000), methyl ethyl ketone was added to the benzene/THF mixture to achieve a homogenous solution. The solutions were mixed at 50 °C for 72 h, then placed inside an air-tight desiccator, transferred into a Millrock LD85 lyophilizer, and freeze-dried without exposure to air for one week. The concentration of salt in the electrolytes is specified by r defined as the ratio of LiTFSI (287.09 g/mol) and PEO (44.05 g/repeat unit). Thus r is the molar ratio of Li^+ ions to ethylene oxide moieties, $r = [\text{Li}^+]/[\text{EO}]$, without accounting for the —OH end groups on each of the chains. (The extent to which oxygen atoms in the end groups participate in coordination with lithium relative to the oxygen atoms in the main chain is not known at this point.) r was held fixed at 0.085 for all samples. The ionic conductivity of PEO/LiTFSI mixtures is peaked in the vicinity of this salt concentration [15,16]. It is customary in the literature of solid electrolytes to use the term n, the molar ratio of EO to Li ions, to describe salt concentration. The value of n in our samples, with no end group corrections, is 11.76

2.2. Electrochemical measurements

Conductivity cells, similar to those designed by Lascaud et al. [15], were built to enable examination of samples with a wide range of viscosities. An important difference is that the diameters of the upper and lower electrodes in our cells were 8 and 10 mm, respectively. The unequal area electrodes were useful for loading samples with widely different mechanical properties, from watery liquids to semi-crystalline solids.

Table 1
Characteristics of the polymers used in this study.

Polymer	M (kg/mol)	PDI	[EO]/chain
PEO(0.2)	0.19	1.01	4
PEO(0.6)	0.64	1.03	15
PEO(1.0)	1.0	1.10	23
PEO(2.0)	2.0	1.10	45
PEO(4.0)	4.0	1.03	91
PEO(10)	10	1.05	2.3×10^2
PEO(20)	20	1.10	4.5×10^2
PEO(50)	50	1.19	1.1×10^3
PEO(360)	360	1.12	8.2×10^3
PEO(5000)	5000	–	1.13×10^5

To facilitate sample loading, the electrolyte was placed on the bottom electrode and heated to 100 °C in the glovebox. In most cases, this resulted in a sample of uniform thickness on the electrode. PEO(360)/LiTFSI and PEO(5000)/LiTFSI showed too great a resistance to flow even at elevated temperature. They were pressed into pellets of appropriate size and loaded into the conductivity cells. Sample thicknesses (error $= \pm 1$ μm) were determined by subtracting the thicknesses of the lower and upper electrodes from the overall assembled cell thickness. The thicknesses ranged from 0.8 to 2.2 mm.

A home-made temperature controlled box was used to house the cells during the electrochemical experiments. The AC impedance spectroscopy measurements, performed using a 16-channel Bio-Logic VMP3 potentiostat, were made across the frequency range 1 MHz to 10 Hz at a peak-to-peak amplitude voltage of 20 mV. The electrolyte resistance, R, was determined by the low-frequency minimum on a Nyquist impedance plot. Measurements were made at a series of temperatures with a minimum of 3 h equilibration at each temperature. All data presented in this work are from cooling runs.

Calculating the sample conductivity from the measured resistance R requires knowledge of both the electrode separation, L, and the effective cross-sectional area, A_{eff}. To find the effective area of a conductivity cell with two unequally sized electrodes, the experimental set-up was modeled in COMSOL Multiphysics. Solving Laplace's equation for the primary current distribution in the polymer electrolyte yielded the steady state current, I, through the electrodes as a function of applied voltage, V and assumed value of electrolyte conductivity, σ_{model}. These were used to calculate the effective cross-sectional area by $A_{\text{eff}} = LI/(V\sigma_{\text{model}})$. The linearity of Laplace's equation means that A_{eff} depends only on geometry and is independent of V and σ_{model}. The numerical data were found to obey the empirical equation,

$$A_{\text{eff}} = 0.0023*L^3-0.0291*L^2+0.135*L+0.498. \tag{1}$$

Sample conductivity, σ, was calculated using $\sigma = L/(A_{\text{eff}}R)$. Three samples from each electrolyte were tested, with error bars of data points representing the standard deviation. The exception was PEO(5000)/LiTFSI, for which only one sample was run. The accuracy of our procedure was verified using an aqueous KCl conductivity standard. Conductivity measurements were made between 330 and 368 K. The PEO/LiTFSI mixtures are in the amorphous state in this temperature

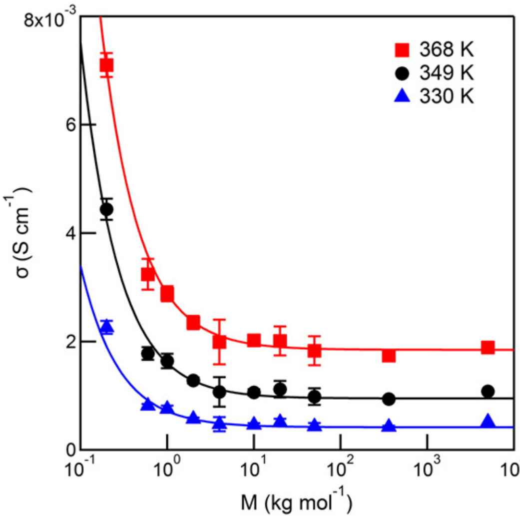

Fig. 1. Ionic conductivity, σ, as a function of molecular weight, M, of PEO/LiTFSI electrolytes with $r = 0.085$ at three temperatures. The curves represent the fit to Eq. (2).

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