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Ion conduction mechanism of nanocomposite polymer electrolytes comprised of polyethyleneimine–lithium bis(trifluoromethylsulfonyl)imide and silica

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ABSTRACT

Ion conduction in poly (ethyleneimine):lithium bis(trifluoromethylsulfonyl)imide (PEI:LiTFSI) electrolytes containing 7 wt% of 7-nm-diameter SiO_2 nanoparticles was investigated at different salt concentrations. These PEI:LiTFSI:SiO_2 electrolytes were prepared with molar ratios from 400 to 20 and were characterized by impedance spectroscopy, differential scanning calorimetry, and viscosity measurements. The ionic conductivity had a maximum at the molar ratio 100, and the temperature dependence of the conductivity showed Arrhenius behavior. The molar conductivity first increased and then decreased as a function of increasing salt concentration. The viscosity and the glass transition temperature exhibited sequentially a maximum and a minimum as the salt concentration increased. The Walden product had a maximum at a molar ratio of 100. Both segmental flexibility and free-ion concentration influenced the conduction mechanism when SiO_2 nanoparticles were present in the electrolyte. A molar ratio of 100 yielded the largest free-ion concentration and segmental flexibility.

1. Introduction

About 30 to 40% of the primary energy in the World is used in buildings, specifically for heating, cooling, lighting, ventilation and appliances [1]. Clearly energy savings is of large importance for the buildings sector, and electrochromic (EC) windows stand out as one of the key technologies [2]. EC windows, also referred to as “smart windows”, were suggested about thirty years ago [3,4] and are presently gaining popularity [5]. These windows make it possible to regulate the inflow of visible light and solar energy into buildings, and hence they can yield energy efficiency together with indoor comfort [6–10].

The EC windows that are currently introduced have a five-layer structure [5,11–13] with a centrally positioned electrolyte connecting two oxide thin films with EC properties, and with transparent electrical conductors surrounding the EC oxides. The electrolyte can be an inorganic thin film, a polymer electrolyte, or an ionic liquid. The two EC materials can be one tungsten oxide film (coloring under charge insertion, *i.e.*, cathodically) and another nickel-oxide-based film (coloring under charge extraction, *i.e.*, anodically) [14]. Fig. 1 illustrates a polymer-based device, wherein the five-layer structure is positioned between two substrates of glass or plastic. Also shown are the electrical contacts that allow insertion/extraction of electrons from the transparent electrodes as well as charge-balancing ions from the electrolyte. The device operation can be resembled to that of an electrical battery with a charging state that corresponds to the intensity of the optical absorption [5].

EC windows embodying polymer electrolytes [15,16] have a number of advantages over all-oxide-based options, as elaborated in a recent paper of ours [17], and we have made in-depth studies of a “model electrolyte” comprised of poly (ethyleneimine) and lithium bis(trifluoromethylsulfonyl)imide (PEI:LiTFSI). This electrolyte was characterized with regard to the salt concentration dependence on viscosity, glass transition temperature, and ionic conductivity [18]. Furthermore, equivalent-circuit modeling of PEI:LiTFSI electrolytes was carried out, and it was shown that ionic conductivity and ion-pair relaxation are two parts of the same process [19]. The ion conduction mechanism of these electrolytes was investigated at different salt concentrations and temperatures, and effects of ion concentration and mobility on the conductivity were elucidated [20]. Subsequent to this fundamental characterization of the PEI:LiTFSI electrolytes, they were functionalized by the addition of dispersed nanoparticles of In_2O_3:Sn (ITO) and/or SiO_2 [21,22]. The ITO nanoparticles absorbed near-infrared radiation without compromising the optical clarity in the visible range [21]. Ionic conduction and optical properties of PEI:LiTFSI:SiO_2 nanocomposite polymer electrolytes with different amounts of nano-sized SiO_2 particles were examined [22], and it was demonstrated that the SiO_2 nanoparticles could yield an enhancement of the ionic conductivity by almost an order of magnitude without degradation of the

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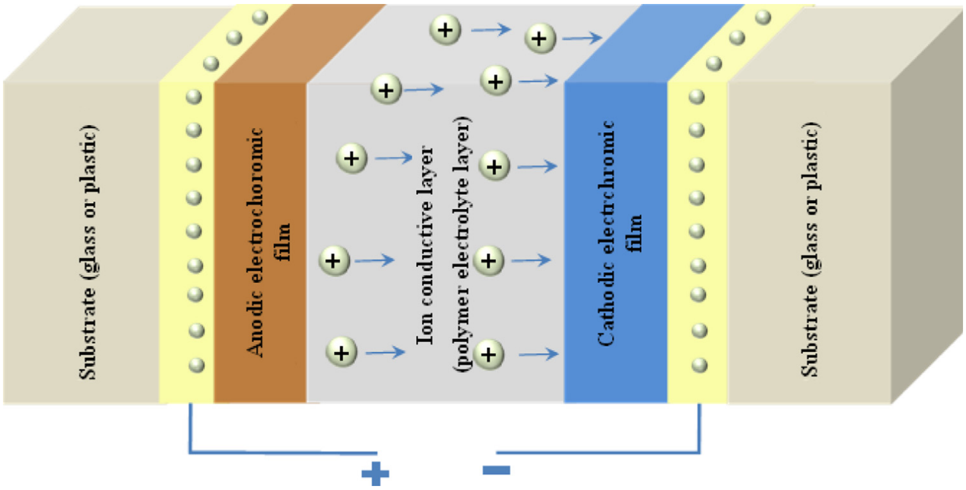

Fig. 1. Schematic illustration of an electrochromic window with a polymer electrolyte.

optical properties. Finally, we studied EC devices based on tungsten oxide and nickel oxide and incorporating PEI:LiTFSI:propylene carbonate:ethylene carbonate, functionalized by adding SiO_2 and ITO, and demonstrated that the nanoparticles improved the coloration dynamics [17].

Polymers and ions can interact with each other in various ways, and this interaction will influence the conduction mechanism of polymer electrolytes [23–25]. A number of studies have shown that an addition of nanoparticles to the polymer electrolyte can provide high ionic conductivity along with suitable optical, mechanical, and thermal properties [26]. In particular it has been shown that SiO_2 nanoparticles (fumed silica) are able to improve the conduction of nanocomposite polymer electrolytes [27–30]. The proton conduction mechanism of SiO_2-doped PEI-based polymer electrolytes has been studied [28,29] but, to the best of our knowledge, the influence of SiO_2 on the conduction in PEI:LiTFSI:SiO_2 electrolytes with different salt concentrations, which is the object of this paper, has not been investigated.

2. Experimental

PEI (10000 g/mol) with 99% purity was obtained from Alfa–Aesar. LiTFSI [*i.e.*, $LiN(CF_3SO_2)_2$, 99.95%] and 7-nm-diameter fumed silica with surface area 390 m^2/g were purchased from Sigma–Aldrich. Anhydrous methanol (CH_3OH, 99.8%) was obtained from Merck. PEI was dried before use at 65 °C and 10^{-1} mbar for 48 h. LiTFSI was used after drying at 150 °C and 10^{-1} mbar for 72 h. Fumed silica and methanol were used as received. All materials were stored under dry conditions (<1 ppm H_2O) in an argon-filled glove box.

LiTFSI was added to the methanol and the solution was stirred until the salt dissolved. SiO_2 and PEI were then added sequentially to the solution. The SiO_2 concentration was kept constant at 7 wt%. The nanocomposite polymer electrolytes were prepared at [N]:[Li] molar ratios, denoted *n*, of 400, 200, 100, 50, and 20. The molar ratio was determined as described elsewhere [18]. All materials were mixed until homogeneous solutions were obtained. Solutions were kept at 65 °C and 10^{-1} mbar for 48 h to remove the methanol and for drying the samples. All samples were stored under dry conditions, as mentioned above.

The ionic conductivity of PEI:LiTFSI:SiO_2 electrolytes with different salt concentrations was recorded between 20 and 70 °C in an argon-filled glove box. The measurements were carried out with a Novocontrol BDC-N dielectric interface and a Solartron 1260 frequency response analyzer by sweeping over 48 points in the frequency range 10^{-2}–10^7 Hz. The applied ac voltage was chosen to be 1 V in order to avoid noise at high frequencies. The temperature was kept constant during each measurement to an accuracy of 0.5 °C. The sample cell consisted of two parallel stainless steel electrodes, with a diameter of 20 mm, separated by a ring-shaped Teflon spacer with 1 mm radial thickness and 3.1 mm height. The frequency dependent conductivity $\sigma(\omega)$ was obtained from the measured conductance $Y'(\omega)$ of the electrolytes via the equation

$$\sigma(\omega) = \frac{d}{A} Y'(\omega), \tag{1}$$

where *d* and *A* are thickness and cross-sectional area of the electrolyte, respectively.

Differential scanning calorimetry was performed with a Mettler Toledo DSC 30 instrument in order to determine glass transition temperatures of the electrolytes. The electrolytes were first heated, then cooled, and again heated between −100 and +80 °C. Heating and cooling rates were 10 and 5 °C/min, respectively.

Viscosity measurements were done on a Brookfield DV-II + Pro viscometer with cone/plate spindle at 40, 50, 60, and 70 °C to a temperature accuracy of 1 °C. Recordings at room temperature could not be performed because of the high viscosity of the samples.

3. Results and discussion

Fig. 2 reports the real part of the conductivity as a function of frequency for PEI:LiTFSI:SiO_2 electrolytes with molar ratios 20, 50,100,

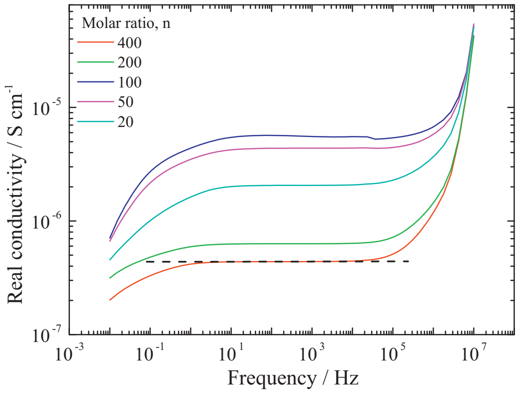

Fig. 2. Conductivity at room temperature as a function of frequency for PEI:LiTFSI:SiO_2 electrolytes with different molar ratios, *n*.