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Conductivities of electrolytes based on PEI-*b*-PEO-*b*-PEI triblock copolymers with lithium and copper TFSI salts

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Abstract

Tri block-copolymer poly(iminoethylene)-*b*-poly(oxyethylene)-*b*-poly(iminoethylene) with a poly(oxyethylene) central block (PEI-*b*-PEO-*b*-PEI) were used as a "dual" matrix for polymer electrolytes having selectivity for hard cations (Li^+/PEO) in one phase and for soft cations (Cu^{2+}/PEI) in the other. Conductivity measurements were recorded for 20:1, 12:1 and 8:1 coordinating atom (O or/and N) to cation (Li^+, Cu^{2+}) ratios, for each of the three complexes studied: PEI-*b*-PEO-LiTFSI-*b*-PEI, PEI-$Cu(TFSI)_2$-*b*-PEO-*b*-PEI-$Cu(TFSI)_2$ and PEI-$Cu(TFSI)_2$-*b*-PEO-LiTFSI-*b*-PEI-$Cu(TFSI)_2$. For either low (20 °C) or high temperature (80 °C) the highest conductivity was given by the polymer electrolyte based on $Cu(TFSI)_2$ with $N/Cu^{2+}=20{:}1$ (10^{-6}, respectively 2×10^{-4} S cm^{-1}). In the present paper, the conductivity evolution is discussed in relation with the polymer structure, the type and the concentration of the salt and the thermal behavior of our systems.

Keywords: Poly(iminoethylene)-*b*-poly(oxyethylene)-*b*-poly(iminoethylene); LiTFSI; $Cu(TFSI)_2$; Polymer electrolyte; Conductivity

1. Introduction

Among the poly(ether)s, poly(oxyethylene) has, to date, been the most widely studied polymer matrix, due to its superior solvation power for a wide range of salts [1,2], with more affinity for hard cations (Li^+, etc.). Beside primary and secondary batteries and ambient temperature fuel cells, polymer electrolytes may be used in practical applications as: electrochromic devices, modified electrodes/sensors, solid-state reference electrodes, supercapacitors, etc. Recent work on PEO complexed with divalent metal salts [2–6] has been motivated by general interest in the electrochemistry of divalent ions. Even if the relatively low cationic conductivity can limit their applicability, these complexes still are promising candidates for the development of optical devices and sensors, where the use of less expensive and less reactive metals than lithium, may be highly desirable [2,3,6].

PEO-containing copper salts systems have been studied by several research groups [2–6]. Conductivity values of 10^{-4} S cm^{-1} around 100 °C, and 10^{-5} S cm^{-1} at room temperature were recorded by Bonino et al. [3] for their systems based on poly(oxyethylene)-copper triflate (Cu^{2+}). Improved conductivity values at room temperature were obtained for similar systems, poly(oxyethylene)-copper triflate, by Lewandowski and Stępniak [5] by the addition of tetramethylene sulfone (TMS). By addition of 20% wt TMS, an increase of the bulk conductivity at room temperature from 10^{-5} S cm^{-1} to almost 5×10^{-4} S cm^{-1} was recorded.

Linear poly(iminoethylene) (PEI) is the nitrogen analogue of poly(oxyethylene), and was also used as a matrix for polymer electrolytes. The polymer electrolytes based on linear poly(iminoethylene) with different lithium salts have low conductivity values at room temperature, 1×10^{-8} S cm^{-1}, to reach 1×10^{-3} S cm^{-1} at 150 °C [7–9]. A higher conductivity value at

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room temperature (1×10^{-4} S cm^{-1}) was announced by Tanaka et al. [8] for their systems based on PEI–PEO poly-blends with $LiClO_4$.

The rich literature that exists in the area of polymer electrolytes also contains a few studies of polymer electrolytes based on di- or tri-block-copolymers of PEO complexed with different lithium salts [2,10–13]. Poly(oxystyrene)-poly(oxyethylene)-LiTFSI and poly(alyl-glycidil-ether)-poly(oxyethylene)-LiTFSI have been studied by Alloin et al. and very low conductivity values were found [11]. Allcock et al. have recorded conductivity values around 10^{-4} S cm^{-1} at high temperatures and between 7.6 10^{-6} and 10^{-6} S cm^{-1} at room temperature for poly(phosphazene)-poly(oxyethylene)-lithium triflate and cross-linked poly(alyl-glycidil-ether)-poly(oxyethylene) + LiTFSI [13]. Until now, none of the homo or copolymer studied show real advantages over PEO.

In a previous paper [14], we have reported the synthesis and characterization of a triblock copolymer "dual" matrix and its polymer electrolytes. The new "dual" matrix, poly(iminoethylene)-*b*-poly(oxyethylene)-*b*-poly(iminoethylene), PEI-*b*-PEO-*b*-PEI, with selectivity for hard cations (Li^+/PEO) in one phase and for soft cations (Cu^{2+}/PEI) in the other could be used as a reference electrode or in electrochromic devices. Our previous study showed a phase separation in the presence and in the absence of perflorosulfonimide salts and specific interactions between each cation (Li^+, Cu^{2+}) and the triblock-copolymer. The present paper deals with the ionic conductivity in relation to the salt nature, the salt concentration and the thermal behavior of our new systems.

2. Experimental section

2.1. Materials

The synthesis of the linear poly(iminoethylene)-*b*-poly(oxyethylene)-*b*-poly(iminoethylene) copolymer with a molecular weight of 3400–4000 g mol^{-1} and 1:4 ratio PEO/PEI was following the procedure described in detail in a previous paper [14]. The copolymer is crystalline, very hygroscopic and forms crystal hydrates with water. It is stable until ~400 °C.

In our studies, lithium and copper tetrafluorosulfonimide salts were used. LiTFSI is a commercial product and $Cu(TFSI)_2$ was synthesized in our laboratory. The "designer" imide anion $[CF_3SO_2)_2N]^-$ abbreviated TFSI [15,16] is one of the weakest bases known. In addition, it is extremely stable and with its low rotation barriers around the SNS bond, is considered as a "plasticizing salt".

2.2. Polymer electrolytes preparation

After several days of drying under vacuum, appropriate quantities of PEI-*b*-PEO-*b*-PEI copolymer and different quantities of LiTFSI, or $Cu(TFSI)_2$ salts, were dispersed in 7 ml of dry methanol, under agitation, in an inert atmosphere (dry box), so that the ratio between the coordinating atoms and cation was 20:1, 12:1 and 8:1 for both O/Li^+ and N/Cu^{2+}. After 24 h of agitation at 40 °C, a yellow solution of LiTFSI-block-copolymer, and blue solutions of both $Cu(TFSI)_2$-block-copolymer and LiTFSI/$Cu(TFSI)_2$ salts mixture-block-copolymer were obtained. The solvent was evaporated under inert atmosphere at room temperature and the pasty polymer electrolytes were dried under vacuum for 72 h.

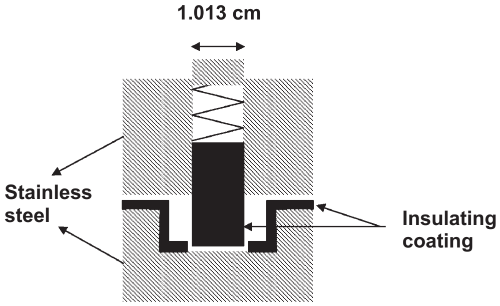
2.3. Methods

The DSC measurements were performed on a Perkin-Elmer Pyris 1 system. The samples were sealed in aluminum pans in the glove box and were examined at a scanning rate of 5 °C min^{-1} by applying two heating scans and one cooling scan. The temperature range was −150 °C to 120 °C.

The polymer electrolytes' conductivities were measured by Ac impedance. The experiments were carried out on a Hewlett-Packard HP4192A frequency response analyzer, over the range 13 MHz–10 Hz, by using a symmetrical cell with two stainless-steel blocking electrodes. The conductivity cell temperature was adjusted by a digitally controlled bath. It was maintained for 3 h at 90 °C before starting the measurements and for 30 min at each temperature before recording the conductivity value. The global system was driven by a computer using a program developed in our laboratory. The conductivity values were recorded at every 5 °C in both cooling and heating processes between 20 °C and 90 °C.

2.4. Cell "designer" for conductivity measurements

The conductivity measurements were performed in a stainless steel cell formed by a metallic cylinder, including a cylindrical central cavity and a piston which closes the cavity (Scheme 1). The metallic cylinder and the piston represent the two electrodes of the cell. A piece of plastic is introduced into the cavity and leaves visible only 1 cm^2 disc from the cavity's bottom. The section of the piston is slightly less than 1 cm^2. The cell is designed to assure a uniform distribution of the polymer electrolyte into the cavity, to adjust the thickness of the sample as a function of its viscosity and to remove the excess material. In order to measure the conductivity of our sample, a certain quantity of the polymer electrolyte was placed into the central cavity and was heated for several hours (to melt and uniformly display into the cavity) before applying the piston and closing the cell. A tablet sample was formed "in situ" between the piston and the bottom of the cavity. For conductivity



Scheme 1. Cell used for conductivity measurements of the polymer eletrolytes.