



Study of ageing effects in polymer-in-salt electrolytes based on poly (acrylonitrile-co-butyl acrylate) and lithium salts



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ABSTRACT

Polymer electrolytes composed of an acrylonitrile and butyl acrylate copolymer poly(AN-co-BuA) with addition of LiN(CF₃SO₂)₂ (LiTFSI) or LiI and LiTFSI salt mixture are studied by impedance spectroscopy, DSC, Raman spectroscopy, X-ray diffraction, SEM and TEM. Impedance study shows that the ionic conductivity of the electrolytes containing LiTFSI is strongly dependent on the salt content and transition from “salt-in-polymer” to “polymer-in-salt” regime is observed at high salt content. Gradual changes of physical properties of the studied polymer electrolytes are observed in the course of their prolonged storage under argon atmosphere. These include the increase of glass transition temperature and decrease of ionic conductivity. In order to study the effects of this ageing process, measurements on samples of electrolyte films were repeated after several months. Precipitation of salt, which occurred at the nanometer length scale is observed with the aid of electron microscopy in electrolytes containing more than 84 wt.% of salt. Crystalline salt is not observed in electrolytes with lower amount of salt – however, the results indicate the structural changes of salt aggregates, which strongly influence transport of ions through the electrolyte. For preparation of electrolytes with mixed LiTFSI and LiI salts, a mixture of salts (16 wt.% LiI, 84 wt.% LiTFSI) is used, which exhibits the lowest melting temperature. The electrolyte comprising poly(AN-co-BuA) and 65 wt.% of the salt mixture exhibits high ionic conductivity and turns out to be more stable than electrolytes comprising only LiTFSI salt.

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1. Introduction

Solid electrolyte, composed of polymeric matrix and lithium salt, exhibiting ionic conductivity sufficiently high for practical application in a rechargeable Li-ion battery is one of the goals that scientists in this field have been trying to attain for decades [1]. In a traditional approach, a small amount of salt is dissolved in polymer matrix. In order to promote dissociation of ions, polymers with relatively high dielectric constant and cation complexing ability are usually applied. These include polymers based on ethylene oxide, which attract most of scientific interest [2]. For polyether based electrolytes, transport of ions is supported by segmental movement of polymer chains. Therefore, conductivity of such

systems decreases strongly upon cooling to glass transition temperature or during crystallization, which immobilizes segments of the chain [3]. Fillers [4] or additional solvents [5] have been added in order to suppress crystallinity and soften polymer matrix. Another approach to design of polymer electrolyte is to use polymer matrix, which does not provide strong interactions with salt, but instead ensures a good structural skeleton for the membrane. One type of such systems are polymers soaked with organic solvent or ionic liquid [6,7]. Obtaining of a homogeneous electrolyte is possible also for alkali salts with high melting temperature. In electrolytes obtained by solvent casting method, overcooled amorphous state of salt is initially stabilized by the solvent, and after its removal by interactions with the polymer matrix.

The systems, in which content of salt is much higher than in traditional polymer electrolytes, have been introduced by Angell et al. [8,9] and described as “polymer-in-salt”. Such electrolytes combine good mechanical properties of the polymer with high conductivity of the solid electrolyte. The lithium transport number

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in polymer-in-salt electrolytes is also expected to be high [9] making them an attractive material for development of polymer lithium-ion batteries.

Preserving amorphous state of salt can be achieved by interactions between salt and polymer matrix. Among different polymers, polyacrylonitrile PAN has been found to be promising for that application. Ferry et al. [10] has shown that PAN is involved in dissolution of the salt and hence suppression of salt precipitation process. However, it has been presented that “polymer in salt” systems can be prepared also using nonpolar polymers hosts such as polystyrene [11]. In such a case, dissolution of salt was enabled by addition of small amount of Al₂O₃ filler, which provided Lewis acid-base interactions. Other concepts of electrolytes with high amount of salt include “solvent in salt” and “ionic liquid in salt”. For electrolytes of the first type, high lithium transference number of 0.73 and excellent electrochemical stability as well as cyclic performance in prototype cells have been reported [12]. Promising results were published also for “ionic liquids in salt” [13] for which high content of salt of about 70% weight seems optimal concerning the value of ionic conductivity. However, performance of such systems as solid electrolyte may be limited by their complex phase behavior [14].

After years of research, it has been well accepted that an efficient ionic transport mechanism in a “polymer-in-salt” electrolyte should be associated with a high degree of ionic aggregation. Therefore, a salt with low dissociation energy is required to provide the ionic species in such a system [10]. There is also agreement concerning the mechanism proposed for the ion cluster/aggregate transport in these electrolytes [10,15,16]. It has been suggested that the enhancement of the ionic conductivity observed in electrolytes rich in salt reflects dynamic connectivity effects in a phase-separated electrolyte passing through a “smeared” percolation threshold. According to Bushkova et al. [15], when a critical cluster concentration is achieved, all separate single clusters come into contact with each other, thus forming an infinite cluster and promoting a fast cationic transport process within the entire electrolyte.

Study of model binary systems, like 3-hydroxypropionitrile with LiI salt, has shown, that at very high salt concentrations, a large number of ionic clusters/aggregates connect with each other to form long ionic chains, providing percolation pathways for ion transport in the electrolyte [17]. In study of polyacrylonitrile (PAN)/LiCF₃SO₃ electrolyte Forsyth et al. [18] proposed a model for connectivity percolation of the ionic clusters, in which ion transport becomes decoupled from the segmental motion of the matrix. High ionic conductivity was observed for electrolytes with salt content between 45 and 66 wt.% [19]. Decoupling of ion transport from motions of PAN matrix has been reported also by Voigt and van Wüllen [20] for a wide range of concentration of LiBF₄ salt. However, in this case the electrolyte contained also DMSO solvent and Al₂O₃ filler, which provided strong competition for interactions with lithium cation and BF₄⁻ anion, respectively.

In description of temperature dependence of ionic conductivity for electrolytes rich in salt, either Arrhenius or Vogel-Tammann-Fulcher (VTF) model may be considered. As transport in those systems relies mostly on ion-ion interactions, one can assume high degree of decoupling of ion transport from segmental movements of polymer chains. If “static” structure of ion clusters is considered, movement of ions in these domains depends on activation energy for individual jumps between the sites, which justifies application of Arrhenius-type dependence:

$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{-\Delta E}{k_B T}\right) \quad (1)$$

However, the clusters of molten salt can be also considered as a disordered amorphous medium, in which the structure is subjected to dynamic changes. In such a case, above the glass

transition temperature, the transport is supported by redistribution of free volume, thus indicating VTF-type temperature dependence of conductivity:

$$\sigma = \frac{\sigma_0}{T} \exp\left(\frac{-B}{T - T_0}\right) \quad (2)$$

For polymer electrolytes parameter B, often described as “pseudo-activation energy”, is considered to be dependent on ratio between free volume required for jump to next site and the volume of solvation cage [21]. For some polymer electrolytes, transition from VTF type to Arrhenius type of thermal dependence of ionic conductivity has been observed, caused by increasing concentration of salt in the electrolyte [22]. This effect has been generally attributed to precipitation of salt.

Previously, we have reported that the random copolymers of acrylonitrile and butyl acrylate seem to be a convenient matrix for polymer-in-salt electrolytes [23] due to their high flexibility and good solubility in volatile solvents, easily removable from the solvent-cast films. Poly(AN-co-BuA) copolymers with LiN(CF₃SO₂)₂ salt (LiTFSI) form flexible membranes exhibiting glass transition temperature (around 0 °C) significantly lower than that of the parent copolymer (about 40 °C). We observed that with an increase of the salt content in the system, the plasticizing effect of LiTFSI is enhanced and ionic conductivity increases, reaching about 10⁻⁵ S/cm at room temperature [24]. Furthermore, the system with high content of salt was characterized by high Li⁺ transference numbers between 0.5 and 0.8 [23]. Our results indicated that the poly(AN-co-BuA) matrix provides good solubility also for other salts, such as LiI.

Copolymers of acrylonitrile intended for application in electrolyte for rechargeable batteries were studied also by other authors. For copolymers of acrylonitrile and *n*-(4-(aminosulfonyl) phenyl) acrylamide ASPAA mixed with lithium perchlorate a maximum ionic conductivity of about 1 × 10⁻⁵ S/cm at room temperature has been obtained. [25]. In this case, participation of carbonyl units from ASPAA in coordination and transport of lithium cations has been proposed. For electrolytes composed of blend of poly(acrylonitrile-co-vinyl ethylene carbonate) poly(AN-co-VEC) and ethylene vinyl acetate copolymer (EVA) with lithium triflate LiCF₃SO₃ an exceptionally high transference number of 0.74 has been reported [26]. In addition to reasonable value of ionic conductivity (6 × 10⁻⁵ S/cm), this indicates possibility of practical application of such polymer hosts in Li-ion cells. A detailed report on properties of electrolytes based on poly(butadiene-acrylonitrile) with a wide range of LiAsF₆ salt concentration has been published by Yaroslavtseva and Bushkova [27]. It has been suggested that the transport based on ion-ion interactions may strongly depend on geometry of conduction paths created by ionic agglomerates. The authors also indicated that, above certain salt concentration, the electrolytes with weak interaction between polymer and salt behave in similar way as supercooled liquids, which makes their properties strongly dependent on sample history.

In this work, we provide a detailed description of physical properties of rubbery solids obtained by mixing random copolymers poly(AN-co-BuA) and LiTFSI. The selection of LiTFSI salt as ion source was based on its plasticizing properties and structural flexibility of its anion [28]. Electrolytes with LiTFSI anions have usually relatively low value of glass transition temperature in respect to electrolytes with other anion types [29]. Materials ranging from pure copolymer, through low salt content systems corresponding to traditional “salt-in-polymer” electrolyte, to “polymer-in-salt” electrolytes with high salt content (up to 95 wt.%) have been studied. In order to enhance ionic conductivity, for selected compositions of electrolytes LiTFSI salt has been

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