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Novel polymer electrolytes based on thermoplastic polyurethane and ionic liquid/lithium bis(trifluoromethanesulfonyl)imide/propylene carbonate salt system

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ABSTRACT

Polymer electrolytes were prepared from thermoplastic polyurethane with addition of mixture of ionic liquid N-ethyl(methylether)-N-methylpyrrolidinium trifluoromethanesulfonimmide (PYRA₁₂₀₁TFSI), lithium bis(trifluoromethanesulfoneimide) salt and propylene carbonate. The electrolytes characterization was performed by thermogravimetric analysis, differential scanning calorimetry and scanning electron microscopy. The electrical properties were investigated in detail by impedance spectroscopy with the aid of equivalent circuit fitting of the impedance spectra. A model describing temperature evolution of ionic conductivity and the properties of electrolyte/blocking electrode interface was developed. The electrolytes have good self-standing characteristics, and also a sufficient level of thermal stability and a fairly good electrochemical window. The ionic conductivity increases with increasing amount of mixture, and the character of temperature dependence of conductivity indicates decoupling of ion transport from polymer matrix. For studied system, the highest value of ionic conductivity measured at room temperature was 10⁻⁴ S cm⁻¹.

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1. Introduction

Among the technological challenges in developing electrochemical devices, such as lithium ion batteries, fuel cells and supercapacitors, there are the growing concerns about the safety issues. The high vapor pressure and liquid state of the conventional electrolytes represent a major problem, because they pose significant fire hazards under abuse conditions and can be the cause of dangerous leakages that decrease the safety and the lifetime of the devices [1]. Therefore, in the last years the research effort has been focused on liquid-free electrolytes [1,2]. Solid polymer electrolytes could replace the liquid electrolyte allowing the fabrication of flexible, compact, solid state structures, free from leaks and available in a variety of geometries [3]. This can result in significant advantages in weight, volume, and packaging cost [2]. The main problem related to these solid polymer electrolytes is their relatively low conductivity at ambient temperature between 10^{-8} and 10^{-5} S cm⁻¹ [4], which may be due to many factors like, e.g. degree of crystallinity of the polymeric matrix, salt concentration and methodology for film deposition.

In a more recent approach, gel electrolytes have been used as alternative between solid polymer electrolyte and conventional liquid electrolyte, because they can exhibit conductivity as high as 10^{-3} S cm⁻¹ at ambient temperature [5,6], which is comparable to that of the liquid electrolytes. A gel electrolyte is generally formed by confining a certain amount of liquid electrolyte in a polymer framework. The polymer acts as the medium to maintain the physical strength and shape of the electrolyte, and the percolated liquid medium (confined electrolyte) enables the transportation of lithium ions through the membrane [2]. Thermoplastic polyurethane (TPU) has been largely employed as polymeric matrix for the preparation of polymer electrolytes [7–22]. Because of its excellent mechanical properties, TPU may provide an alternative to the widely used PVdF and its copolymers for the preparation of gel electrolytes.

Recently, the ionic liquids (i.e. molten salts at ambient temperature) have attracted a wide interest because of their unique

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characteristics, including high thermal stability, no flammability and high ionic conductivity [23–25]. These properties make them the ideal candidates for the preparation of solid and gel electrolytes.

In this work we present the characterization of gel polymer electrolytes based on thermoplastic polyurethane and a solution of the ionic liquid N-ethyl(methylether)-N-methylpyrrolidinium trifluoromethanesulfonimmide (PYRA₁₂₀₁TFSI) and LiTFSI, by varying the ratio between the polymer and the salt. A fixed amount of propylene carbonate (PC) was added, as it was recently reported to improve the electrochemical performances of some systems (PVdF-HFP) gelled with ionic liquids without substantial alteration of the thermal and anodic stability of the electrolyte [26]. The electrolytes were characterized from a thermal and electrochemical point of view.

2. Experimental

2.1. Preparation of the electrolytes

Polymer electrolytes were prepared with thermoplastic polyurethane (TPU) (Irogram PS455-203-Huntsman Polyurethanes) and a mixture of ionic liquid/LiTFSI/propylene carbonate (PC) salt system (MIX) in a wide range of concentration. The NMR data (not shown) confirm what reported by Koerner et al. [27] and by Powers et al. [28]. Irogram PS455-203 contains $\sim 10\%$ of aromatic diisocyanate (MDI) (hard segment), ~32% aliphatic and cyclo-aliphatic dicarboxylic acids and \sim 58% aliphatic diols (soft segments). The Irogram M_w , obtained by gel permeation chromatography (GPC), is around 120,000 g mol⁻¹. The ionic liquid PYRA₁₂₀₁TFSI was synthesized as reported elsewhere [29]. The MIX solution with molality of 0.41 mol kg⁻¹ was prepared by adding a proper amount of LiTFSI and PC (5 wt% in relation to the salt), previously dissolved in tetrahydrofuran (THF), to the purified ionic liquid. The solution was dried at 70 °C in order to completely remove the solvent. Amounts of this stock solution were added to a TPU solution (THF) to prepare electrolytes with MIX content between 10 wt% and 70 wt%. Films of the electrolytes were prepared by the casting technique. Each operation was carried out in a dry-box (MBraun, O₂ < 1 ppm, H₂O < 1 ppm) under argon atmosphere. All films were found to be self-sustaining with good mechanical characteristics.

2.2. Methods of characterization

Differential Scanning Calorimetry (DSC) measurements were performed with a 2910 MDSC (TA Instruments) by using aluminium pans, at a rate of 20 °C min⁻¹ under nitrogen purge. Such a rate was chosen in order to magnify thermal events that can hardly be detected at lower rates. Three heating and cooling scans were performed from -100 °C to 200 °C in order to remove volatile residues during the first heating run. High resolution thermogravimetric analysis (TGA) measurements were carried out at 5 °C min⁻¹ under N₂ purge with a resolution factor of 5 in a 2950 TGA (TA Instruments). Scanning Electron Microscopy (SEM) was performed at different magnifications by a Cambridge Stereoscan 200 microscope on gold sputtered samples.

In order to determine the electrical properties of the electrolytes, impedance spectroscopy sweeps were carried out by using a frequency response analyser (FRA Solartron 1255), connected to an electrochemical interface (Solartron 1287), over the frequency range 0.1 Hz to 1 MHz at a voltage of 50 mV. The impedance scans were performed onto a two stainless steel electrodes cell (area of 2 cm^2) in the temperature range between -20 and $100 \,^\circ$ C. The impedance spectra were analyzed by the nonlinear least squares fit-



Fig. 1. (a) Thermogravimetry (TGA) curves of selected TPU:(IL+LiTFSI+PC) electrolytes and pure TPU (upper part) and the derivative, dm/dT, of the signal (lower part). (b) Normalized weight loss related to each decomposition step (see text).

ting of an equivalent circuit with the aid of program Firdarvn [30]. The quality of fits was judged by the root-mean-square residual.

Linear voltammetry was performed in a setup based on 7050 potentiostat AMEL INSTRUMENTS with a three electrodes cell, in which stainless steel was both the counter and working electrodes, and Ag was the reference one.

3. Results and discussion

3.1. TGA

The thermal degradation of TPUs is a complex process which, generally, occurs in two stages [31–33]. The first stage is mainly related to the breaking of rigid segments, and involves the dissociation of urethane in the original isocyanate and chain extensor, that then form primary amine, alkenes and carbon dioxide. During the second stage, in which the flexible segments are involved, both depolycondensation and polyol degradation mechanisms take

place [31]. Unfortunately, preliminary conventional TGA measurements could not yield a clear splitting between the two stages, thus, high resolution TGA was required to improve their separation. In Fig. 1a the Hi-Res TGA trace and its derivative vs. T signal (DTG) recorded on pure TPU and selected TPU:MIX electrolytes are shown. Pure TPU is thermally stable up to \sim 270 °C, temperature at which the first of the consecutive thermal decomposition events begins. Since good resolution cannot be achieved neither by optimizing Hi-Res TGA measurements, for every decomposition step a rough estimation of both final and initial positions was made by taking the flex points falling between two successive decompositions on the weight signal. These points correspond to the temperatures of minima in the TGA derivative curve (see insert in Fig. 1a). The weight losses obtained on pure TPU from the analysis based on this criterion are 38% and 59% for the first and second stages, respectively. For what concerns the TPU:MIX electrolytes, the decomposition occurs in three different stages: the first and the second stages are related to the breakdown of the rigid and flexible TPU segments, respectively, while the third one can be ascribed to the collapse of the IL + LiTFSI + PC mixture. In order to investigate in detail the mutual influence of TPU and IL+LiTFSI+PC mixture on each decomposition stage, every weight loss belonging both to the first and second stages was normalized to the TPU molar fraction while the weight losses pertinent to the third decomposition step were normalizes to the MIX content. Fig. 1b reports the normalized weight losses for the three decomposition stages vs. composition. The results indicate that the presence of the IL + LiTFSI + PC does not significantly affect the thermal stability of the electrolytes (1st decomposition stage) at least within the normalized experimental error. Conversely, for the second stage, a significant increase of the normalized weight loss with the MIX is observed. For what concerns the third decomposition stage, in the range of MIX content from 20 to 70 wt% the normalized weight loss remains almost unchanged.

The observed dependence could be reasonably explained in the following way: the interaction between the MIX solution and the rigid segments of TPU is quite weak and does not appreciably affect the decomposition stage in which the hard parts of the polymer are involved. Instead, the stronger interaction between MIX solution and flexible segments affects the second stage of the decomposition where these segments are concerned. Finally, since the thermal degradation of the whole polymer has occurred, the remaining MIX solution is only slightly affected by the matrix residues and its weight loss keeps nearly constant.

3.2. DSC

Besides the low temperature $T_{\rm g}$ related to the flexible segments, polyurethanes with considerable concentrations of rigid segments could show up to three endothermic effects in the DSC curve [34]. The first one (t_1), taking place around 70–100 °C is related to the rigid segments short-range order; the second one (t_2) , falling in the temperature range between 120 and 170 °C is due to the long-range order, and the third one (t_3) , that can be



Fig. 2. Second heating run DSC curves of pure TPU and electrolyte containing 70% of IL + LiTFSI + PC mixture (the temperature range was restricted for better visualization of glass transitions phenomena). Values of glass transition Tg for the entire studied range of electrolyte composition are presented as insert. Filled squares are related to the T_g of polymer and empty circles to the T_g of IL + LiTFSI + PC.

detected at temperatures above 200 °C and is related to the rigid segments micro-crystallinity. The examined Huntsman TPU contains just 10% of rigid segments [27,28] and its DSC trace (Fig.2) highlights a tiny endothermic effect around 135 °C [35], related to a long-range order. Moreover, just one glass transition at -42 °C, already reported by some authors [28] and ascribed to the flexible segments (Fig. 2) was detected.

In the TPU:MIX system the glass transition temperature initially decreased as a function of MIX content, from -42 °C (pure TPU) to $-73 \circ C$ (50 wt% of MIX), because of the plasticizing effect played by the ionic liquid. When a higher amount of MIX is added (56 and 70 wt%), besides an increase of the T_g values, a second glass transition at about -90 °C, likely due to the segregated MIX solution, is observed. The effect of increasing T_{g} with high salt contents is widely known for polymer electrolytes, as in the case of poly(ethylene oxide) base system [36].

3.3. SEM

The surface of pure TPU as well as of the electrolytes with a small amount of salt was found to be flat and smooth. As an example, the surface of electrolyte with a 10 wt% fraction of IL + LiTFSI + PC mixture is presented in Fig. 3. The surface of electrolytes with a significant amount of salt (up to 50 wt% fraction of MIX) exhibited some small pores, which could origin from the last phase of solvent drying process. Besides those features, however, it was smooth and even.



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Fig. 3. Scanning electron microscope (SEM) photographs of surface of TPU:(IL+LiTFSI+PC) electrolytes. Ratios denote the weight fraction of TPU to mixture.

The surface of the electrolytes with the weight fraction of mixture larger than 50% was found to be more rough, as presented in Fig. 3 for the electrolyte containing 56 wt% of the MIX. A granular pattern has been observed in the microphotographs. Arrangement of these grains into larger domains may be interpreted as segregation of mixture or its components on the surface of the electrolyte, as confirmed by the appearance of a second glass transition on the corresponding DSC traces. The presence of such a surface layer may be the cause of differences in electrical properties of the electrolyte/electrode interface between dilute and concentrated electrolytes, as reported below. It should be noted, that although presence of MIX on the surface of the electrolyte may have some impact on its electrochemical stability, it does also improve adhesion to the electrodes, which improves the value of ionic conductivity.

3.4. Models of impedance spectra

The equivalent circuits used for modelling of the impedance spectra consisted of the following elements: resistors (denoted as *R*), capacitors (denoted as *C*) and constant phase elements (*P*). The complex capacitance can be described by $C^*(\omega) = P(i\omega/\omega_0)^{n-1}$, where $\omega_0 = 1 \text{ s}^{-1}$, *i* is the imaginary unit, and the magnitude of CPE element, *P*, is expressed in farads. When the exponent *n* was found to be equal 0.5, the element was described as *W* (Warburg impedance).

It was found that, in the case of all investigated electrolytes, the impedance spectra can be well reproduced by the equivalent circuit shown in Fig. 4. This equivalent circuit consists of two segments, one related to the bulk properties of electrolyte and the other to the properties of the interface [37,38]. Impedance spectra of electrolytes comprising 10, 50 and 70 wt% of MIX, measured at 0°C and



Fig. 4. Equivalent circuit used for modeling of impedance of TPU:(IL+LiTFSI+PC) electrolytes. Cross-hatched symbols denote constant phase elements (CPE), *W* – the Warburg impedance.

80 °C were presented in Fig. 5.

3.4.1. The bulk properties of the electrolyte

The branch related to the electrolyte consists of three elements $C_{\rm h}$, *P* and *R* connected in parallel. In the complex plane plot of the impedance, the response of this branch is given by a semicircle observed in the high/middle frequency range (Fig. 5). In the experimental data of studied system, the whole semicircle was observed well only at low temperature (see Fig. 5, electrolyte with 10 wt% MIX measured at 0 °C). At high temperature only the low frequency part of this semicircle was observed in the characteristic frequency range (Fig. 5, results for 80 °C). The capacitor C_h is related to the high frequency value of dielectric function of the electrolyte, ε , and represents the "geometrical" capacitance of the sample. From results measured for pure TPU, a value of ε equal 5.4 has been obtained at 70 °C, which is close to the values reported by other authors for polyurethanes based on the same isocyanate [39,40]. For the majority of studied electrolytes, the value of this element could be calculated with reasonable accuracy only for low temperatures $(-20 \circ C \text{ and } -10 \circ C)$. The constant phase element P represents fre-



Fig. 5. Selected impedance spectra of TPU:(IL+LiTFSI+PC) electrolytes plotted in complex plane representation. Solid lines represent fit with equivalent circuit from Fig. 4.

quency dependence of ionic conductivity typical of disordered ion conductors. For the investigated electrolytes, the value of exponent n obtained for this element varied between 0.6 and 0.5. This value could be fitted only at low temperature, and was kept constant when fitting the spectra measured at high temperature. The resistor R represents the "bulk" (dc) ionic conductivity of the electrolyte. The value of this element could be fitted well within the whole investigated temperature range for all studied electrolytes.

3.4.2. The properties of the interface

The branch which models the interfacial phenomena (observed in the complex impedance plot as an inclined spur following the semicircle at the low frequency side) consisted of two parts: (i) the constant phase element P_d represents the double layer at the electrolyte/electrode interface, that is connected in parallel to a second part (ii) which contains resistor R_a , Warburg impedance W_a and capacitor C_a linked in series. This last part may be interpreted in terms of partial adsorption of charge at the interface [37], or the presence of two different charge carriers [41]. It should be noted that the equivalent circuit used for the description of interfacial properties of the discussed system is similar to one previously used for fitting of impedance spectra of PEO:LiTFSI electrolytes [42].

At low temperature, for electrolytes with high amount of polymer (see Fig. 5, 10 wt% MIX at 0 °C) a simplified version of the circuit was used including only the W_a element, as the values of resistor R_a and capacitor C_a could not be fitted with reasonable accuracy due to limited experimental frequency window (see for example Fig. 5, 10 wt% MIX at 0 °C). For all electrolytes, gradual changes of the parameters describing the model with the temperature were observed. On heating, the value of element P_{d} related to capacitance of the double layer increased, which can indicate improvement of contact between electrolyte and stainless steel electrodes. A simplified version of the circuit, including only P_d , W_a and R_a elements, was used to fit the spectra measured at the upper limit of investigated temperature range (Fig. 5, results measured at 80 °C). An identical circuit was obtained also in analysis of impedance data measured for pure MIX and therefore, it may be suspected that the observed effect occurs due to increasing influence of the ionic liquid on the interfacial properties. The value of resistance R_a was found to be higher in electrolytes with lower amount of ionic liquid, which may be the consequence of lower value of ionic conductivity of those electrolytes-or, alternatively, if one refers to the partial absorption model mentioned above, an effect of higher charge transfer resistance at the interfacial layer. This phenomenon is observed in complex plane representation as characteristic "bending" of electrode tail, clearly visible for electrolyte comprising 90 wt% TPU (Fig. 5, $T = 80 \circ C$).

3.5. Ionic conductivity

The mechanism of ion transport in TPU-based electrolytes represents a complex phenomenon because of structural nonhomogeneities of the polymer matrix. The soft and hard segments of TPU may give different interactions with the ions, and therefore the description of charge transport process through the electrolyte depends strongly on the specific structure of polymer matrix.

For gel polymer electrolytes, the temperature dependence of ionic conductivity has often been found to be well described by the VTF function [43]. However, in case of gel electrolytes obtained by the impregnation of TPU with propylene carbonate (PC), most authors reported Arrhenius-type dependence [13,15,44]. This effect is believed to be associated with the improvement of salt dissociation as well as weakening of interaction between charge



Fig. 6. Temperature dependence of ionic conductivity for TPU:(IL+LiTFSI+PC) electrolytes. Conductivities of pure polymer and IL+LiTFSI+PC mixture are presented as reference.

carriers and polymer matrix in the presence of PC. The addition of PC was also reported to greatly improve the value of ionic conductivity.

In some cases, a switch from a VTF-type dependence to an Arrhenius one has been observed for a single system, as a function of the TPU composition [45] or the amount of salt present in the electrolyte [34]. The amount of salt in the electrolyte has a significant impact also on the value of the ionic conductivity. For most TPUbased electrolytes, a maximum has been evidenced at a middle concentration range [7,46]. The occurrence of such a maximum has been related to the interplay between opposing effects. On one side, the number of charge carriers increases with increasing amount of salt. On the other side, the presence of salt increases the glass transition temperature and leads to the decrease of free volume, as well as available coordination sites. In electrolytes containing high amount of salt, the influence of ion pairing has to be also taken into account. This effect seems to be weaker in systems with strong decoupling of ion transport from motions of the polymeric matrix, for example gel electrolytes.

The values of the bulk (dc) ionic conductivity of the studied electrolytes were determined according to the value of the resistor *R* obtained from the fit. The plot of temperature dependence of conductivity is plotted in Fig. 6.

3.5.1. The behavior of the pure TPU

For the pure TPU, the temperature dependence of conductivity can be divided into two sections, above and below 20°C. In the Arrhenius plot, both sections can be fitted with a straight line, which would indicate that they represent two energy activated charge transfer processes [47]. An independent experiment involving polarizing microscope observation simultaneous to impedance measurement (for experimental details see Ref. [48]) has revealed, that upon cooling at 10°C the microscope picture obtained with crossed polarizers changes from dark (corresponding to isotropic amorphous phase) to a bright one. The latter phenomenon is usually related to presence of an ordered phase. It is questionable whether this effect is related to the occurrence of a small amount of crystalline phase (below or at the limit of detection by other experimental methods) or rather to ordering of hard segments of TPU, which arrange into domains. For both cases it can be assumed that the structure of the material in these two temperature regions is different, and that the transport of ions through electrolyte which contains rigid (ordered) domains requires a higher activation energy. An alternative explanation of the observed temperature dependence could be a VTF-type relationship with overlaid effect of phase transition. However, without knowing the ion species that are involved in the conduction process (for pure TPU the main source of charge carriers are impurities from the synthesis process) such a hypothesis cannot be verified.

3.5.2. TPU-based electrolytes

For most electrolytes based on TPU polymer matrix with an addition of IL+LiTFSI+PC mixture, the temperature dependence of conductivity could be fitted well with straight line in the Arrhenius plot, which corresponds to energy activated hopping. This is in agreement with observations of other authors, which indicate that in gel electrolytes obtained by impregnation with PC the charge transport becomes highly decoupled from motions of the polymer matrix [13,15,44]. In some cases, a slight bending of the dependence was observed at around 10 °C (more evident in the electrolytes with 56 and 70 wt% of MIX). The limited temperature range of measured data does not allow to decide if this is an indication of mixed Arrhenius and VTF mechanisms [49] or an influence of transition taking place in the pure TPU matrix, as discussed above. The magnitude of this effect is however much weaker than in the pure TPU, which is in agreement with observations of other authors that the presence of mixture suppresses segregation between hard and soft segments [34]. An alternative explanation of observed deviation of the temperature dependence of the conductivity from Arrhenius one may be also related to changes of interfacial properties. In the temperature range where this effect was observed, in fact, the changes in the parameters of model describing the interfacial layer, for example the magnitude of P_d element, were more pronounced. The stiffening of electrolyte surface upon cooling may have caused partial loss of contact with electrodes.

The conductivity of the electrolytes generally increases with increasing concentration of salt, which seems to provide another indication of decoupling in the studied system [34]. The values of ionic conductivity obtained at 20 °C seem quite promising, in fact for the electrolyte containing 70 wt% of the IL+LiTFSI+PC mixture, the conductivity surpassed 10^{-4} S cm⁻¹. For a fairly homogeneous and electrochemically stable electrolyte with 50 wt% of IL+LiTFSI+PC, a value of about 3×10^{-5} S cm⁻¹ at 20 °C was obtained.

3.5.3. Pure IL + LiTFSI + PC mixture

For the pure IL+LiTFSI+PC mixture, the temperature dependence of conductivity can be fitted with a straight line in the Arrhenius plot. However, the relative width of the studied range of temperature does not allow to indicate if it represents a clear hopping type or a mixed hopping and VTF mechanism. At room temperature, the conductivity exceeds 3×10^{-3} S cm⁻¹. This can be treated as the upper limit of conductivity which could be obtained by further modifications of polymer host in the studied system, assuming that the transport of ions is decoupled from segmental motions of the matrix and therefore the polymer mainly contributes to the self-standing characteristics of the electrolytes.

3.6. Electrochemical stability

The electrochemical stability window is an important parameter that determines the applications of polymer electrolytes in electrochemical devices as lithium ion batteries, supercapacitors and fuel cells. As pointed out in the literature, the main advantage of using ILs in the electrolyte materials is their higher electrochemical stability in comparison with aqueous and several organic systems [50,51]. Fig. 7 shows the electrochemical window for the TPU:(IL+LiTFSI+PC) electrolytes (reference electrode Ag/Ag⁺), in



Fig. 7. Electrochemical window for the TPU:(IL + LiTFSI + PC) electrolytes. Reference electrode Ag/Ag^{+} .

both the anodic and the cathodic sides. The potential limits depend both on the reduction and oxidation potentials of the conducting ions as well as on the electrochemical properties of all the other components, like polymer matrix and the solvent [51]. The electrolytes which contain up to 56% mix have good electrochemical stability with no decomposition reaction occurring before 3.5 V. However, for the electrolyte with 70 wt% MIX the decomposition potential was found to be significantly low. This indicates the need for further study to improve the stability of the studied system, in order to achieve electrochemical window which would enable their use as safe electrolytes (nonvolatile and nonflammable) in electrochemical devices.

4. Conclusions

In this paper we reported on TPU-based electrolytes with ionic liquid. TGA and DSC results indicate that the interaction between the polymer matrix and the MIX occurs mainly via the soft segments of TPU. However, regarding an Arrhenius-type temperature dependence of conductivity the coupling between ion transport and segmental movements of the polymer matrix does not seem to be strong, which can be ascribed to the influence of the PC solvent. This seems to be another advantage of studied system in respect to solvent-free solid polymer electrolytes, in which much stronger decrease of conductivity on approaching the glass transition is observed.

It has been found that an equivalent circuit model can be applied to reproduce the measured impedance spectra in a wide range of electrolyte composition. Analysis of parameters calculated from the fit has indicated, that apart from the temperature dependence of ionic conductivity, also the interfacial properties of the studied system are subjected to considerable changes upon heating.

The studied electrolytes have good self-standing characteristics, sufficient level of thermal stability and fairly good electrochemical window. The obtained values of ionic conductivity at room temperature of 10^{-4} S cm⁻¹ for the electrolyte with 70 wt% of IL + LiTFSI + PC provide a good basis for further research on improving stability and homogeneity of concentrated electrolytes.

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