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Synthesis and properties of polymer electrolytes based on polyurethane elastomer and lithium salts

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Abstract

Polymer solid electrolytes were obtained by swelling the polyurethane elastomer with solutions of lithium salts $LiBF_4$ and $LiClO_4$ in DMSO at different concentration of lithium salt. The swelling effect was found to decrease with the increase in the salt concentration, whereas the ionic conductivity has a maximum of $6–8 \cdot 10^{-4}$ S/cm at 5 wt.% lithium salt. The salt solutions incorporated into the polymer pores have melting points ranging from −10 to 2 °C and deswelling takes place at low temperatures. The obtained polyurethane elastomer materials have a high conductivity and may be promising for use in flexible lithium polymer batteries.

Keywords
polymer solid electrolytes
polyurethane elastomer
swelling effect
ionic conductivity
effect of the salt concentration on swelling and conductivity

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1. Introduction

Lithium batteries have gained high importance at present. They are widely used in portable electronic devices, electric vehicles, various energy storage applications and other fields due to their high energy density and excellent service life [1–3]. However, safety concerns because of the growth of lithium dendrites and the resulting short circuit when using liquid electrolytes significantly complicate further development and limit their use. An alternative solution could be to replace the liquid electrolyte with a solid polymer electrolyte (SPE). In addition, this would help to solve the problems of fire and explosion in liquid electrolytes using organic solvents [4–7].

Ionic conductivity of polymer solid electrolytes occurs via flexible fragments that form an amorphous subsystem (so-called gel phase), whereas hard fragments form crystalline regions of the polymer [3–7]. There are several approaches to increasing the concentration of the amorphous phase: the variation of the concentration or chemical composition of linking functional groups, and the introduction of heterogeneous additives, such as carbon nanotubes or oxide fillers. Swelling of electrolyte solutions may also result in a considerable increase in the concentration of gel phase and the increase in the conductivity [12]. In this case the swelling should not lead to the loss of the mechanical stability of the polymer.

Polyurethane is a promising material as a matrix for creating solid polymer electrolytes. This material has flexible structural designs, can be easily modified (with polymers or fillers), and possesses specific functions (self-healing, protective layer or high adhesion). Owing to these characteristics, it is possible to obtain a higher energy density and use a metal lithium anode in batteries. To date, to our knowledge, most polyurethane-based solid polymer electrolytes have been synthesized using chain extenders, catalysts, and organic solvents, followed by a complex polymerization process.

Genier et al. [9] synthesized a polymer based on polytetrahydrofuran (PTHF) and epoxy resin using a cationic initiator and a photo-initiator. The resulting polymer was impregnated in a $LiBF_4$ salt solution in acetonitrile, followed by drying to constant weight. Despite the long and complicated manufacturing process, the authors managed to obtain a material with ionic conductivity from $8.9 \cdot 10^{-6}$ to $7.8 \cdot 10^{-4}$ S/cm, stability over a wide temperature range, and mechanical strength. Another promising approach to the preparation of solid polymer electrolytes was demonstrated by Zhao et al. [10], who synthesized a pre-polymer by mixing toluene diisocyanate with polypropylene glycol with the addition of the LiTFSI salt dissolved in dimethyl carbonate to the resulting mixture. A chain extender and a catalyst were added to the obtained pre-polymers, after which they were poured into moulds for 7 days until complete polymerization. They managed to achieve the maximum ionic conductivity of $9.6 \cdot 10^{-5}$ S/cm at 55 °C. In addition, the polymer electrolyte had good chain flexibility and thermal stability.

In this work, polyurethane-based ion-conducting polymer electrolytes were prepared using a commercially available pre-polymer based on p-phenylene diisocyanate (P-PDI) and polyether, 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA) curing agent, and lithium salts, $LiBF_4$ and $LiClO_4$, dissolved in dimethyl sulfoxide $(CH_3)_2SO$ (DMSO) by elastomer swelling in solutions with different concentrations of lithium salts. The ionic conductivity of the obtained polymer electrolytes was investigated.

2. Experimental

A quantity of the ADIPRENE® LFP 1950A, a PPDI terminated polyester prepolymer (Crompton Corporation), heated to 50 °C was mixed with a given amount of the MOCA hardener (3,3'-dichloro-4,4'-diaminodiphenylmethane $C_{12}H_{12}N_2Cl_2$, chemically pure, manufactured by JIANGSU XINGYUAN CHEMICAL CO LTD) heated to 110 °C using a DISPERMAT CN Dissolver at 2000 rpm for 30 s for degassing. Next, the resulting liquid mixture was poured into a metal mould and heated for 1 h at 110 °C. Then the mould was cooled to room temperature, and the sample was removed and condensed for 7 days before experiments. The synthesis scheme is presented in Figure 1.

Before preparing electrolytes, lithium salts were dried under low vacuum at 150 °C for 24 h. Next, electrolytes were prepared in DMSO with a given concentration of lithium salts. Swelling of polymers with solutions of lithium salts was carried out in a hermetically sealed vessel for 48 h. Conductivity measurements were carried out in an argon atmosphere using a two-electrode scheme in the frequency range 25 Hz – 1 MHz using an MNIPI E-25 Immittance Meter. Conductivity values were determined from the analysis of Nyquist plots. Differential scanning calorimetry (DSC) was performed on a DSC 204 F1 Phoenix NETZSCH instrument (Germany). Aluminum (Al) crucibles for analysis were pre-calcined at 100 °C. The samples were cooled from 25 °C to –40 °C at a rate of 10 °C/min, kept at –40 °C for 10 min to balance the calorimeter system, then heated to 60 °C at a rate of 10 °C/min. The analysis was carried out under the argon (Ar) flow at a rate of 100 ml/min.

3. Results and Discussion

At first, the attempts were made to introduce the lithium salt $LiBF_4$ and $LiClO_4$ directly into the elastomer matrix on heating of the polymer-salt mixtures. As pure salt turned to be insoluble in the polymer, the experiments were performed on swelling the polymer matrix with the solutions of $LiBF_4$ and $LiClO_4$ in DMSO. The swelling effect was estimated by the relative change in the polymer mass after the storage of the polymer in the solutions $LiBF_4$ or $LiClO_4$ with different concentrations of the salt. The mass of the samples was measured every hour until the constant mass achieved. Results of the swelling experiments are shown in Figure 2. As can be seen, the weight gain monotonically decreases by about 10 times with the increase in the salt concentration in the solutions of $LiBF_4$ or $LiClO_4$ in DMSO from 1 to 15%. This effect was observed earlier for polyelectrolyte hydrogels [10, 11] and can be explained in terms of the modified Flory and Rehner theory [14–16] by the interplay between the entropy contribution, osmotic pressure of the solvent and the salt, and the mechanical strain of the polymeric network caused by the incorporation of the salt solution [14–16].

Therefore, to achieve the highest lithium content in the polymer, solutions with a moderately high concentration of lithium salts should be used.

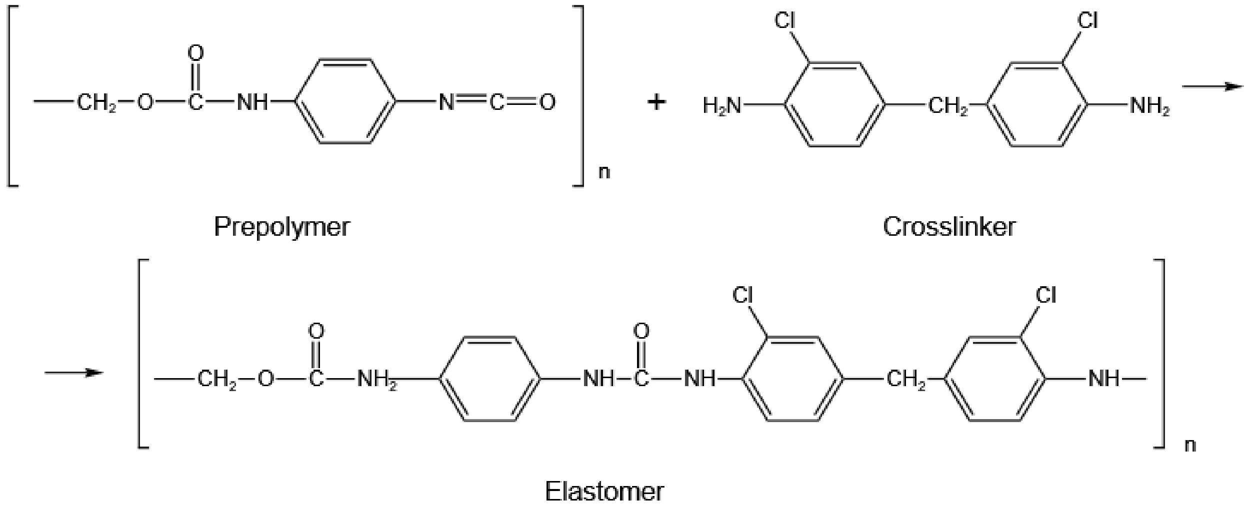

Figure 1 The scheme of the synthesis of polyurethane elastomer, used for the preparation of the polymer solid electrolytes.

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Ionic conductivity data for polymer electrolytes obtained after the swelling are presented in Figure 3. The dependences of the conductivity on the salt concentration in the $LiBF_4$ or $LiClO_4$ solutions used for swelling have a pronounced maximum at 5 wt.% of the salt, both for the lithium tetrafluoroborate and lithium perchlorate. The presence of the maximum can be explained by the competition between two factors: an increase in the total content of lithium in the solution introduced into the bulk of the polymer during swelling, and a decrease in the total amount of the solution entering the polymer with an increase in the salt concentration. The maximum conductivity of polymers obtained by swelling in solutions of lithium salts was $8.6\cdot10^{-4}$ S/cm and $9.1\cdot10^{-4}$ S/cm at 25 °C for $LiBF_4$ and $LiClO_4$ salts, respectively. A change in temperature from 25 to 75 °C does not have a significant effect on the ionic conductivity of solid polymer electrolytes, which is associated with a low value of the activation energy of conductivity of 0.13±0.03 eV.

Low values of the activation energy suggest that the conductivity of the polymers under study is caused by a liquid-like gel phase formed in the pores of the polymer as a result of the swelling of salt solutions in DMSO. In order to investigate thermodynamic properties of the electrolyte phase in polymers, thermal analysis studies were carried out. Figure 4 shows thermal analysis curves obtained for pure DMSO, initial $LiBF_4$ solutions in DMSO, and the polymers after swelling with $LiBF_4$-DMSO solutions of different concentrations.

The heat effect observed on the heating relates to the melting of DMSO or $LiBF_4$-DMSO solutions, as the pure polymer melts at temperatures above 150 °C with partial decomposition. As seen from Figure 5, the intensity of the peak related to the melting process monotonically decreases with the $LiBF_4$ concentration. Comparison of these data with those presented in Figure 2 suggests that the peak intensity changes proportionally to the total amount of the $LiBF_4$-DMSO solution absorbed by the polymer matrix as a result of the swelling. The fraction of the amorphous gel phase also decreases with the $LiBF_4$ concentration, leading to the decrease in the ionic conductivity.

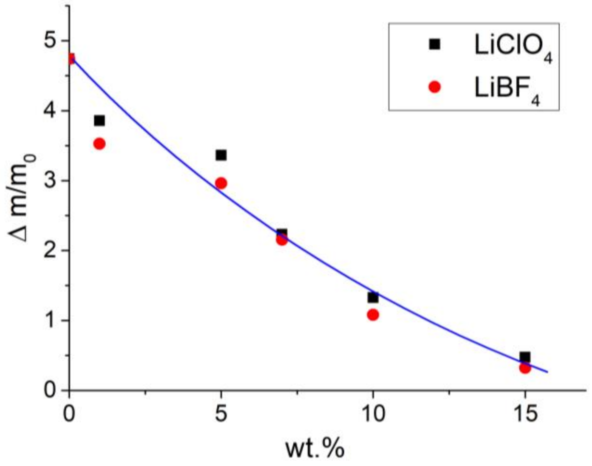

Figure 2 The dependence of the relative change of the elastomer mass on the concentration of $LiBF_4$ in the source solution.

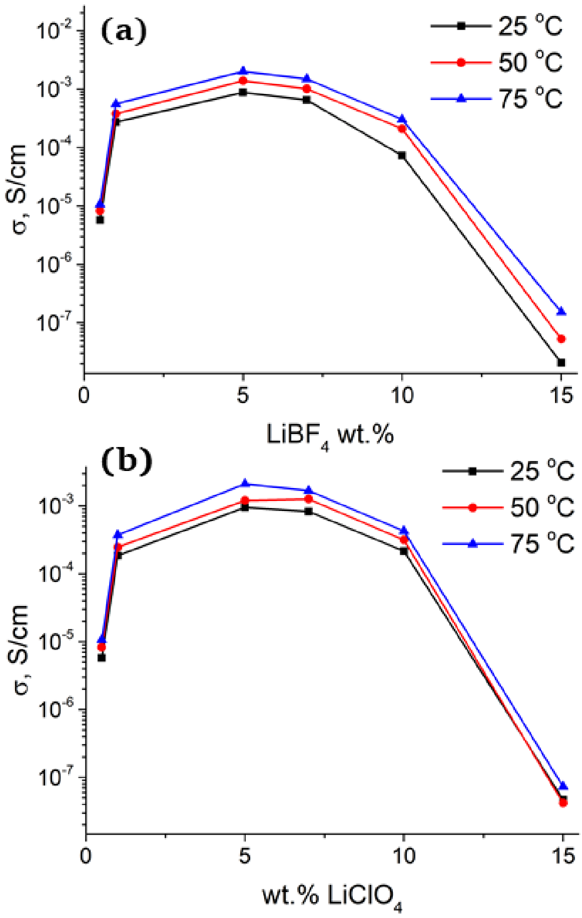

Figure 3 The dependences of the conductivity of polymer electrolytes on the salt concentration in solutions of $LiBF_4$ (a) or $LiClO_4$ (b) used for swelling the polymer.

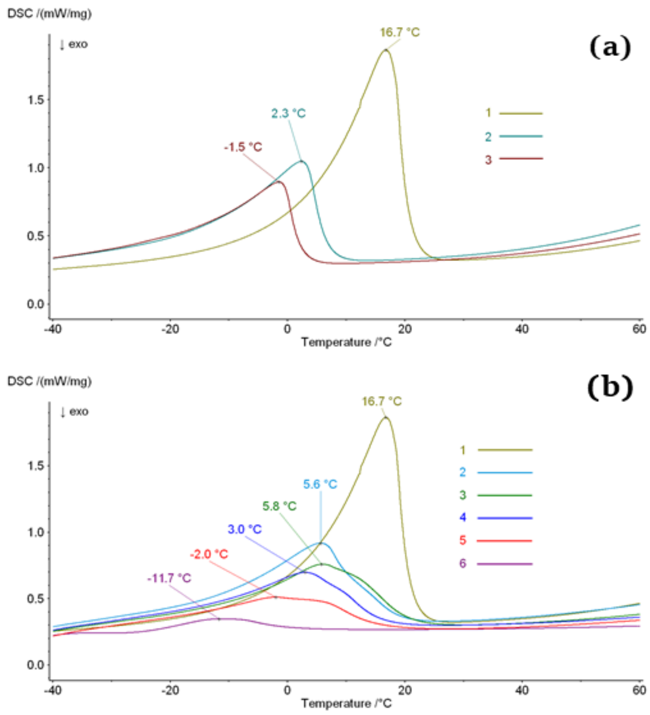

Figure 4 Thermal analysis curves obtained for (a) pure DMSO (curve 1) and $LiBF_4$-DMSO solutions containing 5 and 10 wt.% $LiBF_4$ (curves 2 and 3, respectively); (b) pure DMSO (curve 1) and polymers after swelling with pure DMSO (curve 2) and $LiBF_4$-DMSO solutions containing 5, 7, 10 and 15 wt.% $LiBF_4$ (curves 3, 4, 5 and 6, respectively).

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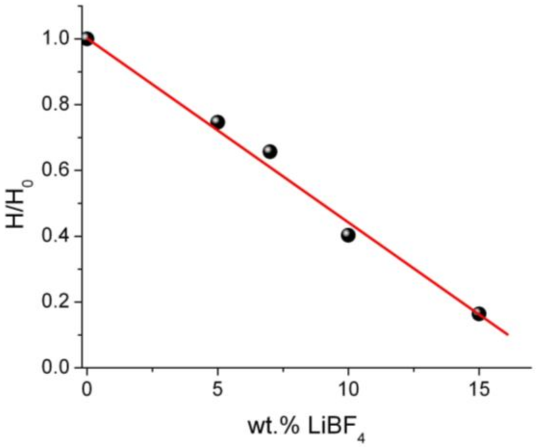

Figure 5 The dependence of the relative change H/H_0 of the melting enthalpy of $LiBF_4$-DMSO solutions included into the polymer matrix (H_0 is the melting enthalpy of pure DMSO in the polymer) on the concentration of $LiBF_4$ in the source solution.

The melting temperatures of $LiBF_4$ solutions are lower than that of pure DMSO, which is typical for solvent-salt systems. The incorporation of pure DMSO into the polymer pores during swelling leads to a noticeable decrease in its melting temperature: the peak temperature of the heat effect related to the melting shifts from 16.7 to 5.6 °C. Such decrease may be explained by a size effect, as an effective "particle" size of DMSO is limited by the volume of pores occupied by DMSO in the polymer matrix. In contrast to pure DMSO, melting temperatures of the salt solutions located in the polymer are close to those for the initial solutions. Moreover, the melting peak splits into two components. It is known that swelling effect increases with temperature [12, 15–17], hence on cooling the effect should vanish. Therefore, experimentally observed thermal analysis data suggest that partial or complete deswelling of the solutions takes place at low temperatures.

4. Limitations

The present study is an initial stage of a complex investigation of polymer solid electrolytes based on polyurethane elastomers. These investigations should include:

– optimization of the polymer structure by variation of the concentration of the cross-linking agent. It will allow one to control the internal free volume, elastic properties of the polymer and its ionic conductivity;

– study of the swelling of other salts with different cations or anions. In particular, it would be of interest to study a series of lithium salts with cosmotropic and chaotropic anions [18] and their influence upon the swelling behaviour and ionic conductivity of the polymer solid electrolytes containing these salts;

– investigation of ionic conductivity of polymer electrolytes in a wide temperature range, especially at low temperatures. Such experiments would give information on the glass transitions of amorphous states of ionic salts in polymers, on deswelling processes, and could also enable estimating the possibilities of the practical applications of the polymer solid electrolytes in flexible lithium batteries.

5. Conclusions

In this work polymer solid electrolytes were obtained by swelling the polyurethane elastomer with solutions of lithium salts $LiBF_4$ and $LiClO_4$ in DMSO at different concentration of lithium salt. The swelling effect was observed for pure DMSO and was found to decrease with the increase in the salt concentration, whereas the ionic conductivity has a maximum at 5 wt.% lithium salt. The salt incorporated into the polymer pores has a melting temperature ranging from –10 to 2 °C. At low temperatures the deswelling effect seems to be present. Nevertheless, the polymer electrolytes obtained in this work have a high ionic conductivity of nearly 10^{-3} S/cm that is comparable with the best polyurethane elastomer analogues [19, 20]. Thus, the obtained polyurethane elastomer membranes showed a high ionic conductivity at room temperature and may be promising for use in flexible lithium polymer batteries.

• Supplementary materials

No supplementary materials are available.

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• Author contributions

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• Conflict of interest

The authors declare no conflict of interest.

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