

Solid Polymer-in-Salt Electrolytes

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There is great interest in the development of highly efficient energy sources for applications such as cellular phones, mobile computers, and also vehicles with electrical propulsion, and among them considerable attention is put on the development of lithium and lithium-ionic batteries. The application in lithium batteries of polymeric electrolytes instead of liquid ones provides a possibility of designing devices of large surfaces and any shape. The high share of anions in the electric charge transfer, which is connected with a drop in the cell power, is a considerable problem.

Electrolytes with high salt content, above 50 wt. %, are one of the ideas for obtaining electrolytes of relatively high anion immobilization. Such electrolytes, called polymer-in-salt-electrolytes (PISE) were first described by Angell et al. (1), and then many works were presented, concerning mainly polyacrylonitrile (PAN) based systems (2,3). The basic difference in the electric charge transfer between these systems and classic salt-in-polymer electrolytes consists in that the ion mobility is not directly connected with the segmental relaxation of the polymer matrix chains and it is assumed to result from the high degree of ion aggregation. For these electrolytes a conduction mechanism is postulated based on the dynamic percolation model with a broad percolation threshold (3).

In this work we present the results of studies on the conductivity of a number of PISE as a function of salt concentration, type of lithium salt anion and chemical structure of the polymer matrix.

Due to the fact that PAN shows solubility in a small number of aprotic solvents such as DMSO and DMF, which are very difficult to remove, PAN based electrolytes were obtained by hot pressing at 150°C and under high pressure. In this work we propose the use of acrylonitrile (AN) and butyl acrylate (BuA) copolymers [poly(AN-co-BuA)] as the matrix, which are well soluble in acetonitrile, a volatile solvent easily removable during the membrane preparation. Figure 1 shows the differences in the conduction ability of systems containing poly(AN-co-BuA) (2:1) and various lithium salts.

The studies carried out show that the conductivity of the electrolytes studied increases with an increase in the salt concentration until reaching a maximum. Beyond this maximum, the conductivity first decreases and then again increases. In this concentration range metastable systems are formed, in which salt crystallization and phase separation occurs within time. The location of the maximum depends on the type of lithium salt. The conductivity as a function of salt concentration for systems comprising LiI and poly(AN-co-BuA) is presented in Figure 2.

DSC studies show that in a majority of composites studied, the introduction of a salt to the polymer causes a considerable decrease in the glass transition T_g value indicating its strong plasticizing effect. Figure 2 presents the dependence of T_g on the salt concentration for the poly(AN-co-BuA) and LiI system.

The decoupling index ($\log R_T$) of the order of 3-5 and shifts in FTIR of the bands of groups present in the polymer $\nu_{C\equiv N}$ and $\nu_{C=O}$ by about 20-30 cm^{-1} indicates a weak interaction of the salt with the matrix. The

transference numbers t_+ (0.5 - 0.8) determined by the electrochemical method indicate an increased share of cations in the electric charge conductance in comparison with classic electrolytes based on salt and polyethers complexes.

REFERENCES

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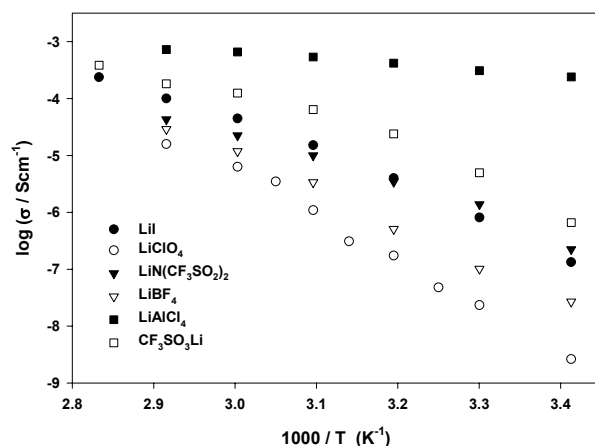


Figure 1. Ionic conductivity of electrolytes based on poly(AN-co-BuA) (2:1) with different lithium salts (1.2 moles of Li^+ per 1 mole of AN monomeric units in the copolymer).

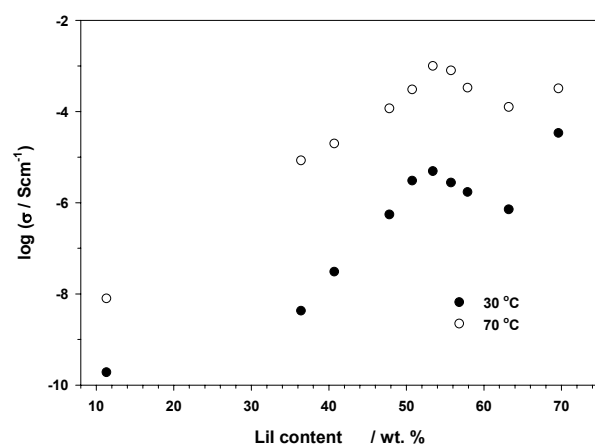


Figure 2. Conductivity isotherms determined at 30 (●) and (○) 70°C for electrolytes comprising poly(AN-co-BuA) and LiI depending on the salt concentration.

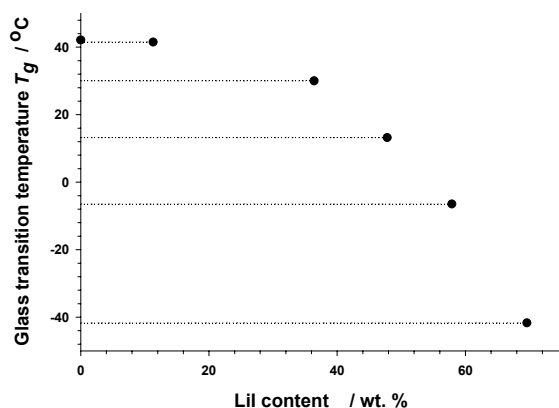


Figure 3. Glass transition temperature T_g of electrolytes comprising poly(AN-co-BuA) and LiI depending on the salt concentration.