

Lithium Doped Polyphosphoester Composite

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Abstract

The effect of lithium triflate on the ionic conductivity of polyphosphoester composite was investigated by electrochemical impedance spectroscopy (EIS). The highest conductivity was obtained for membrane with 15% lithium salt. The ion transport is slow due to the aggregation tendency of ions for composite membrane with higher than 20% lithium salt. The conductivity of all membranes increases linear with the increase of the temperature and shows a thermally activated process.

Introduction

Composite materials find nowadays easily applications in electronic industry. For instance, in solid polymer electrolytes the increase in conductivity is essential and it can be achieved by adding salts, ionic liquids or inorganic nanoparticles in polymer matrix and their amount is an answer to the required improvement.

Various polymer composites with enhanced mechanical, electrical and thermal stability are reported [1, 2]. High value of ionic conductivity at a temperature close to the melting point was reported for solid polymer electrolytes based on poly(ethyleneglycol) (PEG 2000) and lithium perchlorate [3]. Poly(siloxanes), poly(vinylpyrrolidone), poly(acrylates), poly(ethylenesuccinate), poly(vinylalcohol), poly(ethyleneimine), poly(alkylenesulphides) are also a good candidates for solid polymer electrolytes [4].

The aim of this study is to investigate the electrochemical behavior of polyphosphoester composite doped with lithium salt. The effect of lithium triflate on the ionic conductivity was investigated by electrochemical impedance spectroscopy (EIS).

Experimental

Composite membranes M, M1, M2 and M3 contain tris(4-hydroxybutylacrylate)-phosphate: polyphosphoester in a 1.5 :1 %wt ratio and different amounts of lithium salts (Aldrich, LiTf) (5-20 % wt.). LiTf was dissolved in methanol (in minimum quantity) and added to polymer mixture together with 0.15% dispersing agent (polyaniline, PANI) and complexation was completed in an oven at 60°C for 6 h. Photoinitiator Darocure 4265 (3% wt, Cognis) was used to cure the composite mixture. To obtain membranes the composite mixture was cast on a Teflon plate and cured by exposure to UV Lamp type Sunray 400SM. In **Table 1** are presented the notations and composition of the prepared lithium polyphosphoester composite membranes.

Table 1. The notation and composition of prepared membranes.

Membrane notation	LiTf, % wt	Thickness, μm
M1	5	90
M2	10	90
M3	15	110
M4	20	100

Analysis

Jasco FTIR 4200, Miracle ATR spectrometer with ZnSe crystal plate was used to collect the IR spectra. Ionic conductivity of the membranes was determined by the AC impedance spectroscopy. Autolab 302N potentiostat/galvanostat equipped with the FRA2 impedance module was used for EIS determination. At the point where the phase angle is zero (or close to zero) in Bode diagrams, the impedance is pure ohmic and the ionic conductivity can be determined by the following equation (1):

$$\sigma = h / R_b \cdot A \quad (1)$$

where: σ - ionic conductivity, R_b – the resistance corresponding to the angle closest to zero in the Bode diagram, h – the height of the sample between the electrodes, A – the cross-sectional contact area of the measured sample.

Measurements of composite conductivity function of temperature were performed in the range of 25°C to 90°C and the activation energy was calculated using the Arrhenius equation (2):

$$\sigma(T) = \sigma_0 \exp(-E_a / kT) \quad (2)$$

where: σ_0 represents the pre-exponential factor in $S \cdot cm^{-1}$, E_a is the activation energy in eV, and k is the Boltzmann constant.

Results and discussion

The spectra of complexed lithium composite matrix are presented in **Figure 1**. The intensity of the bands associated to P=O (1251 cm^{-1}) and P-O-C (1080 cm^{-1}) bonds presented in composite matrix is reduced and slightly shifted to the lower frequency due to the coordinative bond formed between oxygen atoms from phosphate and ether group and lithium ion. This leads to the formation of complexes between polymer and salt.

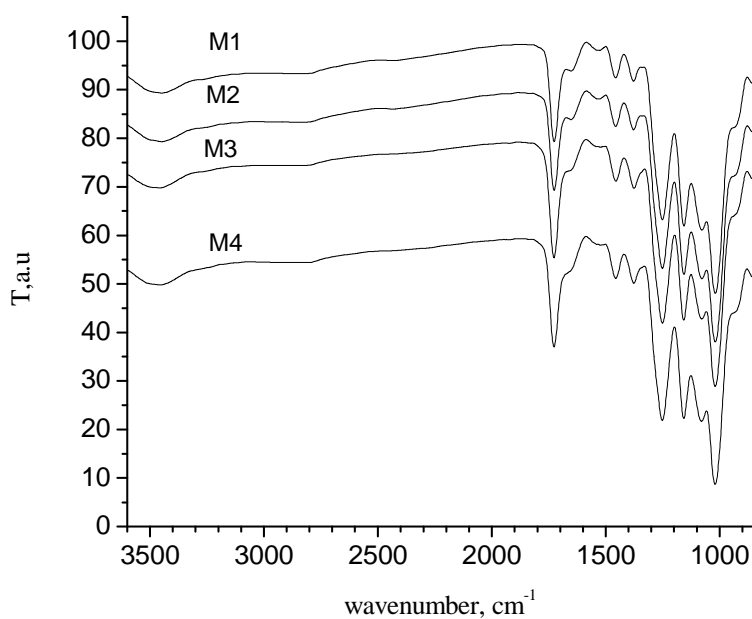


Figure1. ATR. Spectra of membranes M1, M2, M3 and M4.

The highest intensity signal is obtained for M3 membrane and pointed out that the amount of lithium salt added in this membrane is the optimum value.

The ionic conductivity (σ) of membranes was calculated according to Eq. (1), from EIS spectra recorded at Open Circuit Potential (OCP) (**Figure 2a**).

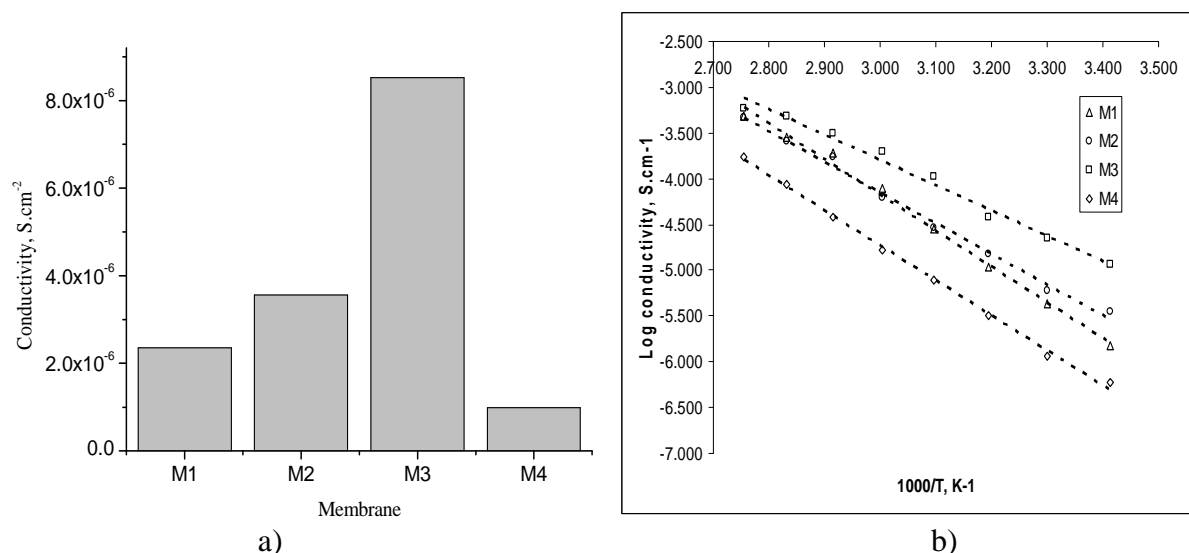


Figure 2. Membrane conductivity a) function of membranes composition at 25°C and b) variation with temperature, plotted in Arrhenius coordinates

The conductivities of membranes increase with LiTf content and above a certain amount decrease. The highest conductivity was obtained for membrane based on M3. The conductivity increases with the lithium salt content from 5 to 15% at room temperature and decreases with the increase of lithium salt content from 15 to 20%. The decrease of conductivity was attributed to the decrease of the available number of charge carriers due to ion aggregation. The M3 membrane presents the highest conductivity of $8.52 \times 10^{-6} \text{ S.cm}^{-1}$.

The conductivity of all membranes increases with the increase of the temperature. The enhanced conductivity arises from the increase of ions and polymer chains mobility. At high temperatures the polymer chains show a high degree of motion and this leads to compensate the unfavorable retarding effect of the ion clouds. The logarithmic plots show a linear variation of the conductivity vs temperature, which is characteristic for a thermally activated process (**Figure 2b**).

The values for activation energy E_a and pre-exponential factor calculated from the linear segment of all membranes are presented in **Table 2**.

Table 2. The pre-exponential factor and activation energy E_a

PANI, ppm	M1	M2	M3	M4
σ_0 , S. cm ⁻¹	7.587	5.910	4.489	6.769
E_a , eV	0.338	0.289	0.238	0.330
R	0.994	0.993	0.989	0.997

The activation energy depends on salt content which is the source of charge carriers in the polymer electrolyte (the decrease of the activation energy is due to the increase number of charge carriers in the polymer electrolyte). It was observed a decrease of activation energy with the increase of salt content till 15% and at 20% salt concentration an increase of

activation energy. With the increase of salt content the number of carriers increase and the conductivity increase. At high ion concentration the number of carriers are diminished and is due to the tendency of ions to aggregate and slow down ion transport.

The σ_0 values explain the composite conductivity as a result of the movement of mobile charge carriers in the membranes. Analyzing the data for the pre-exponential factors it was observed that the increase in E_a (M1 and M2 membranes) tends to be compensating by σ_0 . The compensating effect is mentioned in the literature for a lot of semiconductive materials. The data was fitted by the straight line: $\ln\sigma_0 = 0.119E_a - 1.95$ ($R^2=0.961$) and pointed out the possibility of the carriers to be transported by inter-chain interaction or hopping between localized sites. The slowest macroscopic process will provide the conductivity level.

Conclusion

Membranes based on PANI-polyphosphoester show conductivity by adding lithium salts. The highest conductivity was obtained for membrane with 15% lithium salt. For the composite membrane with 20% salt content the ion transport is slow due to the aggregation tendency of ions. The linear increase of conductivity with the temperature shows a thermally activated process. The correlation between Arrhenius parameters show transport possibility by inter-chain interaction or hopping between localized sites. The macroscopic conductivity will be determined by the slowest process.

Acknowledgements

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