Lithium sulfonated styrene oligomer (LiSSO) as a new class of lithium salt for polymer electrolytes

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Summary

A new class of lithium salt with single-ionic characteristics, lithium sulfonated styrene oligomer (LiSSO) $[(CH_2CHC_6H_5)_7-(CH_2CHC_6H_4SO_3^-Li^+)_2]$, was synthesized and its complex with poly(ethylene oxide) (PEO) was prepared. The maximum ionic conductivity of the PEO/LiSSO complex at 65°C was $2.1x10^{-4}$S/cm at a salt concentration of $[Li^+]/[EO] = 0.20$. The lithium cationic transference number (t_+) of the PEO/LiSSO complex was found to be 0.95, and the polymer electrolyte was electrochemically stable up to 6.2V.

Introduction

High interest in rechargeable lithium batteries has lead to a study on lithium salts that can serve as charge carriers in the electrolyte. The current problems associated with lithium salts used in lithium batteries have stimulated the search for new inexpensive, non-toxic, and stable lithium salts with sufficiently high solubility in suitable solvents to yield high ionic conductivities [1-3].

The lithium salt solutions containing the anions such as ClO_4^-, PF_6^-, AsF_6^-, and BF_4^- have some drawbacks in their properties: they may be thermally unstable [4,5], toxic [6], and show rather poor ionic conductivity [7]. The anions of such salts often influence on the electrochemical stability of the polymer electrolytes undesirably by accelerating the degradation of polymer matrix via their oxidation [8]. The passive layer may also form by the degradation of the anions followed by the reaction with lithium electrode [9]. Moreover, in these bi-ionic type conductors in which both cations and anions contribute to the ionic conduction, current and conductivity usually decay faster with time due to the polarization of the anions when they are applied to a battery driven under d. c. condition [10, 11].

To overcome such drawbacks, some efforts have been made on development of unipolar transport polymer electrolytes, that is, single-ion conductors in which anions are attached to the polymer backbone through covalent bonds and only cations transport [12-15]. However, conductivities in these systems are usually much lower than those reported for the bi-ionic type polymer electrolytes.

The undesirable effects of the anions in bi-ionic type polymer electrolytes as well as low ionic conductivities in single-ion conductors motivated us to develop a new type of lithium salt which is an oligo-organic salt with only lithium cation-conducting characteristics and also with rather a higher ion conductivity. We prepared the lithium sulfonated styrene

oligomer (LiSSO) salt and measured the ionic conductivities of the LiSSO-based polymer electrolytes. The cationic transference number and the electrochemical stability window of these polymer electrolytes were also determined.

Experimental

Sulfonation and neutralization of styrene oligomers

Styrene oligomers $(CH_2CHC_6H_5)_9$ (DAELIM Chemical Co. $\overline{M}_n$ = 940, PDI = 1.09) obtained from anionic polymerization of styrene monomer were used to prepare the sulfonated styrene oligomers. The sulfonation of the styrene oligomers was conducted at 50 °C in 1,2-dichloroethane using acetyl sulfate as a sulfonation agent and the sulfonic acid groups of the sulfonated styrene oligomers were neutralized with 0.1 N standard solution of LiOH in methanol [16]. The reaction scheme for the synthesis of the lithium sulfonated styrene oligomer (LiSSO) is given in Figure 1.
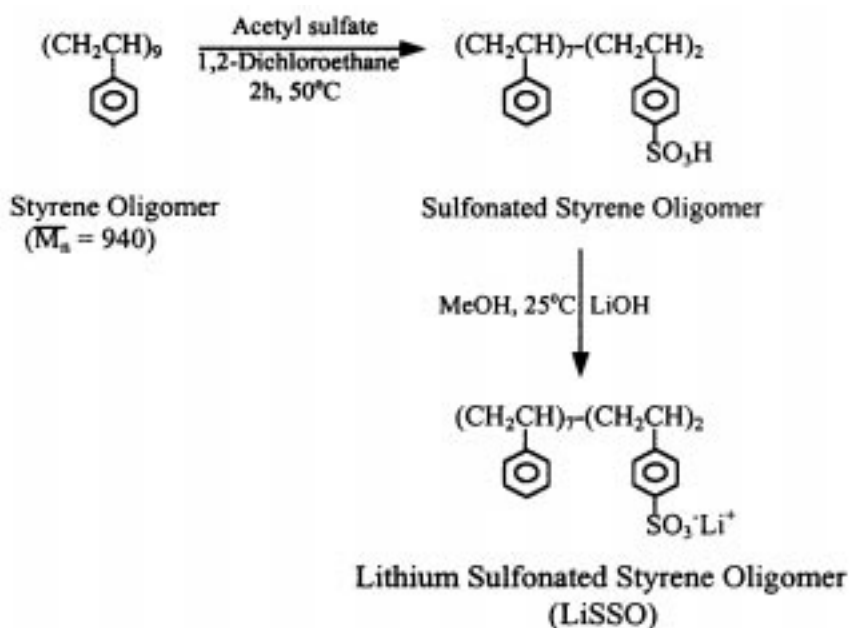

Figure 1. The reaction scheme for synthesis of lithium Sulfonated styrene Oligomer (LiSSO)

Preparation of polymer electrolytes using the LiSSO salt

The PEO (Aldirch, $\overline{M}_n$ = 500,000)/LiSSO mixture was dissolved in acetonitrile. The solution was cast on a Teflon substrate, and the solvent was evaporated slowly under the argon atmosphere for 24 hours in a glove box. The salt concentration in the polymer electrolytes ([Li$^+$]/[EO]) was varied from 0.02 to 0.2.

Impedance measurements

Polymer electrolyte films with the thickness of 150 ~ 250 μm were sandwiched between two stainless steel electrodes (12mm in diameter). Ionic conductivities of the polymer electrolytes were measured by complex impedance analysis using a Solartron 1255 frequency response analyzer coupled to an IBM PS/2 computer over a frequency range of 10MHz ~ 10Hz.

FTIR measurements

Films for infrared measurements were prepared by casting the acetonitrile/polymer electrolyte solutions over KRS-5 windows. After the solvent was evaporated under nitrogen atmosphere for 5 hours, the resulting film was dried at 60 °C for 12 hours under vacuum to completely remove the residual solvent. The FTIR spectra of the films were acquired on a Bomem 102 model fourier transform spectrometer at a resolution of 4cm^{-1}. A minimum of 30 scans were signal-averaged and the spectra were stored on a magnetic disc for further analysis.

DSC measurements

For thermal analysis, differential scanning calorimetry (Thermal analyst 2000, Du Pont) was used. All samples were prepared in the hermetically sealed cells and measurements were taken over a temperature range of -100 to 140°C with a heating rate of 10°C/min under the nitrogen atmosphere.

Results and discussion

Characterization of the LiSSO salt

The sulfonate content of the sulfonated styrene oligomer was determined from the elementary analysis using atomic absorption spectroscopy as well as the titration of the sulfonic acid precursor. It was found to be 22mole%, indicating that in average there are two substituted units per chain of the oligomer.
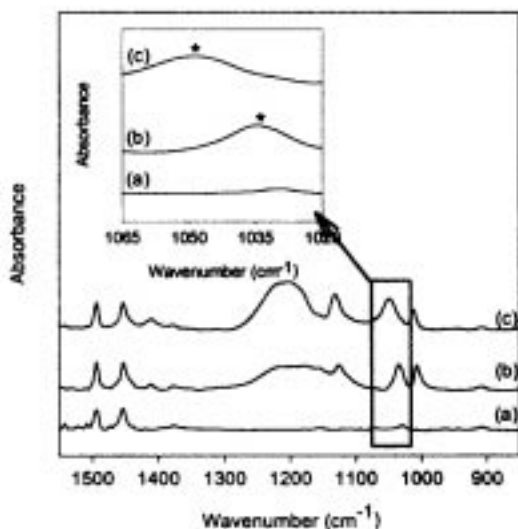

Figure 2. The FTIR spectra of the styrene oligomer, sulfonated styrene oligomer, lithium sulfonated styrene oligomer: (a) styrene oligomer (b) sulfonated styrene oligomer (c) lithium sulfonated styrene oligomer.

Figure 2 (a), 2 (b), and 2 (c) illustrate the FTIR spectra of the three different species, styrene oligomer, the sulfonated styrene oligomer of which composition is (styrene units)/(sulfonated styrene units) = 0.78/0.22, and lithium sulfonated styrene oligomer (LiSSO) respectively. Several bands corresponding to the styrene oligomer appeared in the region between 1400 and 1500cm^{-1}, notably at 1495cm^{-1} (ring stretching vibration of the benzene ring) and 1460cm^{-1} (CH$_2$ scissoring vibration in the aliphatic chains) [17]. Neutralization of the sulfonated styrene oligomer could be confirmed by the IR spectra of the symmetric stretching vibration of the sulfonated ion (1035cm^{-1}) [18]. The peak at 1035 cm^{-1} for the sulfonated styrene oligomer was shifted to the frequency of 1049cm^{-1} when the sulfonated styrene oligomer was neutralized as illustrated in the expanded region of Figure 2.

Effect of the LiSSO content on the ionic conductivity

Figure 3 shows the ionic conductivity isotherms of the PEO/LiSSO complexes as a function of the salt content which can be represented by [Li^{+}]/[EO] ratio. It is found that in general the ionic conductivity initially increases, reaches a maximum, and then falls off with the salt concentration except for the one at high temperature (65°C). The ionic conductivity behavior showing maximum with increase of the salt concentration can be explained in terms of charge carrier concentration and ionic mobility.
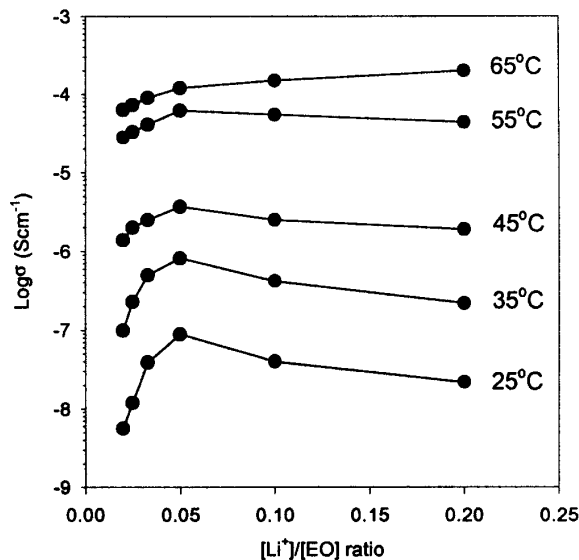

Figure 3. The ionic conductivity isotherms of the PEO/LiSSO complex as a function of salt concentration.

Figure 4 shows a change in the number of free ions per ethylene oxide unit in the PEO/LiSSO system with salt concentration. The number of free ions per ethylene oxide unit can be obtained from the fitted FTIR spectra which is typically illustrated in the inner of Figure 4. The peak at 1036cm^{-1} corresponds to the free ions and another one at 1044cm^{-1} is generated by the ion pairs of LiSSO [19-21]. The number of the charge carrier per ethylene oxide unit is shown to increase with increase of the salt concentration. The addition of the LiSSO into PEO seem to effectively disrupt the crystalline structure of PEO and to result in an increase of the ionic conductivity of the polymer electrolyte in the region of lower salt concentration. The decrease in the ionic conductivity with the salt concentration at the higher

salt concentration region would be a consequence of decrease in the mobility of the charge carrier which can be represented by the glass transition temperature (T_g) of the polymer electrolyte.

Figure 5 shows the glass transition temperatures of the polymer electrolytes as a function of the salt concentration. It is found that the T_g of the polymer electrolytes increase with increase of the salt concentration, which indicates that the mobility of the charge carrier decreases with increase of the salt concentration. The fact that the ionic conductivity shows a maximum at a certain salt concentration is conclusively considered to be due to a competing effect of charge carrier numbers and their mobility on the ionic conductivity in an opposite way.
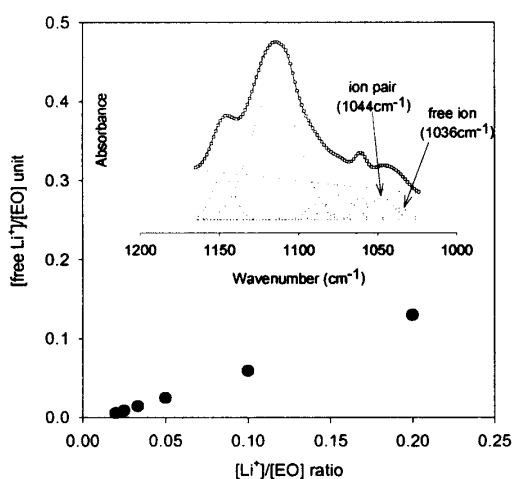

Figure 4. The real amount of lithium free ion per ethylene oxide unit of the PEO/LiSS complex as a function of salt concentration a the ambient temperature.
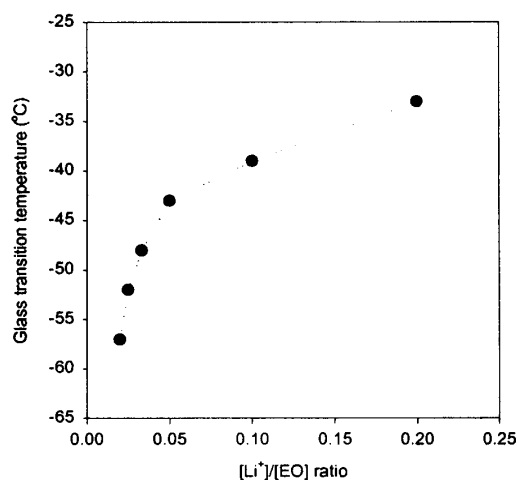
Figure 5. The glass transition temperatures of the PEO/LiSSO complexes as a functio of salt concentration

Lithium transference number of the PEO/LiSSO complex

Figure 6 illustrates an initial a.c. impedance response of the Li/polymer electrolytes/Li cell before inducing polarization (t = 0hr) for the two different polymer electrolytes and also the a.c. impedance response of the cell after a steady-state current has been reached under d.c. polarization (t = 12hr) at 65°C. It is clearly seen that the diameter of the low-frequency semicircle increases very significantly after 12 hours of d.c. polarization for the PEO/LiClO$_4$ system. On the contrary, it is almost unchanged with time for the PEO/LiSSO complex. This semicircle is associated with the Li electrode/polymer electrolyte interface, and thus it is expected that the passivation of Li takes place more severely at the interface between the PEO/LiClO$_4$ and the Li electrode due to the easier degradation of the anions.

Figure 7 shows the current response with time at a given d.c. potential of 20mV. It is found that a constant current reached only after about 12 hours for the PEO/LiClO$_4$ electrolyte, while the current was nearly unchanged during the experiment. The rapid decay of current for the PEO/LiClO$_4$ complex may result from the establishment of a concentration polarization of the anion and also from the growth of the passive layers. Since the sulfonated styrene oligomer anion has a relatively high molecular weight ($\overline{M}_n$ = 1100), the anion movement is quite much restricted and thus the concentration polarization of the anion

becomes less dominant. In addition, the anions might have the resonance-stabilized structure of the sulfonated benzene ring in styrene oligomer units and it would be more stable under electric field.

By using the treatment discussed by Evans et al. [22], the t_+ can be calculated. They were found to be 0.95 and 0.46 for the PEO/LiSSO electrolyte and the PEO/LiClO$_4$ electrolyte respectively. From the result that the t_+ for the PEO/LiSSO electrolyte is almost equal to unity, the LiSSO is demonstrated to have an excellent single-ionic characteristics. This is attributed to the complete restriction in the mobility of the sulfonated styrene oligomer anion.
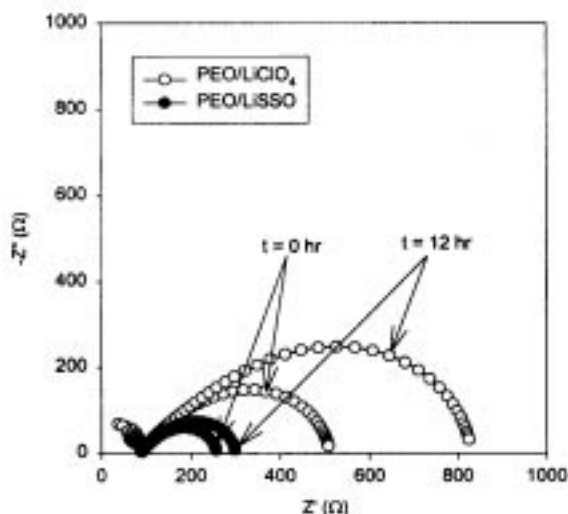

Figure 6. The a.c. impedance spectra of th Li/polymer electrolyte/Li cell at the initia state and after 12 hours of polarization a 65°C (cell area: 2cm × 2cm)

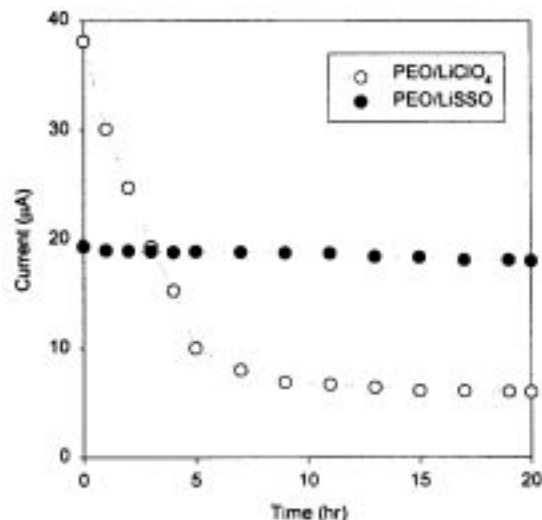

Figure 7. The current response as a functio of time during polarization of the Li/polyme electrolyte/Li cell at 65°C (applied potential 20mV, cell area: 2cm × 2cm).

Electrochemical stability of the PEO/LiSSO complex

For the determination of the anodic limit of the polymer electrolytes, the current-voltage response of an inert test electrode by linear sweep voltammetry was obtained [23]. Figure 8 shows the current-voltage response of the cell based on the PEO/LiSSO or PEO/LiClO$_4$ as an electrolyte and Li as a counter electrode. The PEO/LiSSO complex showed a higher electrochemical stability window (6.2V) than the PEO/LiClO$_4$ system (4.8V).

The onset of significant current at higher voltage for the cell based on the PEO/LiSSO complex indicates that the irreversible oxidation of the anion or the degradation of the polymer chain is more limited for the polymer electrolyte based on the LiSSO anion than that using the perchlorate anion. It is thus proposed that the LiSSO is a promising candidate for the lithium salt of the polymer electrolytes which can be compatible with lithium-intercalation electrodes.
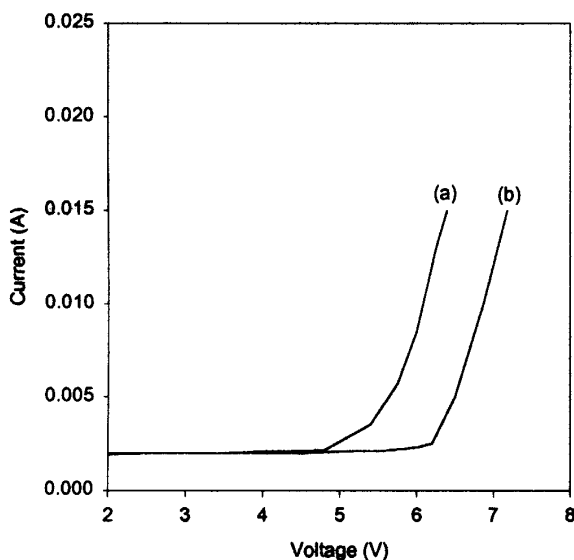
Figure 8. The current response as a function of time during polarization of the Li/polymer electrolyte/Li cell at 65°C (applied potential : 20mV, cell area : 2cm × 2cm).

Acknowledgements

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