

IONIC CONDUCTIVITY IN THE COMPLEXES OF COMB-SHAPED POLYETHER WITH LITHIUM AROMATIC SULFONATE

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ABSTRACT

Complexes of comb-shaped polyether and lithium aromatic sulfonates bearing different negative charge number were prepared by in situ thermal polymerization. Their conductivity depends deeply on salt content, ambient temperature and negative charge number of the added salts. Results show that anions can be partly immobilized by increasing their negative charges at lower temperature. Against discharge time the short circuit current of the battery (Li/complex film/ $\text{Li}_x\text{V}_3\text{O}_8$) is stabilized by increasing the anionic charge number of the complex.

INTRODUCTION

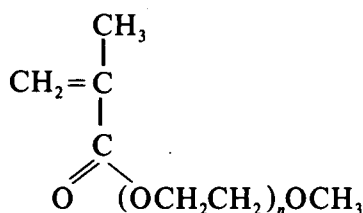
Considerable interests have recently been focused on polymeric solid electrolytes (PSE) due to their potentially practical application in solid electrochemical devices since Armand pointed out that polyether complexes of alkali metal salts could be acted as an ideal candidate electrolyte material^[1]. Since then it has been known that elastic phase provides conduction column and polar group solvates salts, and not longer later it becomes a criterion to design the molecular structure of the polymers used in high-conducting PSEs. So far several PSEs with high conductivity have been reported, and their battery applications have been preliminarily studied as well. Investigations reveal that cationic migration plays more important role than conductivity itself in the properties of the batteries with cation-inserted cathodes^[2]. Thus much effort has been devoted to the study of single-ion conductors although their conductivity is far lower than the anion-mobile systems^[3]. Other convenient attempts to restrain the migration of the anions have also been taken by enlarging their volume^[4] or by enhancing anionic charge number^[5]. Following Bannister's pioneering work, here we report a relatively simple approach towards immobilizing anions by using lithium salt with double-valent anions.

EXPERIMENTAL

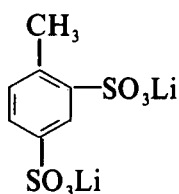
1. Materials

(1) Oligo (oxyethylene) methacrylate (I, MEO_n , where $n=16$) was synthesized as described in our previous work^[6]. Toluene-bisulfonic acid was prepared from toluene according to the standard sulfonation technique^[7], and then

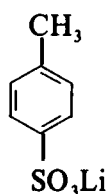
neutralized with equal molar LiOH. The resultant lithium toluenebisulfonate (LTBS, II) was recrystallized from methanol/water mixed-solvent (4:1 in volume),



(I)



(II)



(III)

followed by a dry-treatment under vacuum. Lithium *p*-toluenesulfonate (LTS, III) was obtained by neutralizing *p*-toluenesulfonic acid (purchased from Shanghai Chemical Co.) with LiOH. Lithium salts obtained above are white powder when completely dried.

(2) Complex films were made by in situ thermal polymerization as follows: A calculated amount of MEO_{16} and LTS or LTBS, respectively, together with a given amount of 2,2'-azobisisobutyronitrile (2 mole% vs. MEO_{16}) was dissolved in methanol. The solution was developed in a Teflon plate and allowed to evaporate under nitrogen flow at 80 °C for one day. The remaining viscous solution was further evacuated at 100 °C for another 14h over P_2O_5 in order to carry out thermal polymerization under the condition of complete dryness. The $^1\text{H-NMR}$ and IR spectra of methanol extracts of the resulting complex films show no residual monomers, verifying a complete polymerization. The thickness, generally ranging from 80 to 100 μm , of complex films can readily be governed by modifying both concentration and amount of monomeric solution.

2. Measurements

(1) A Perkin-Elmer DSC-7 Differential Scanning Calorimeter was used to evaluate the glass transition temperature at a heating rate of 10 °C /min under dry nitrogen atmosphere. The T_g was taken as the midpoint temperature of the baseline shift observed during the transition from the glass to the rubber-like state.

(2) Ac conductivity measurement was conducted by an 1100Hz conductometer equipped with a temperature-controlling apparatus in a dry-nitrogen box. After a pre-treatment at 100 °C for 1h the sample was naturally cooled to 20 °C, then was heated to measure the conductivity at various temperatures. In order to reach a thermal equilibrium it is necessary to keep the sample at constant temperature for at least 30 min before each incremental rise.

(3) The batteries composed of (Lithium/complex film/ $\text{Li}_x\text{V}_3\text{O}_8$, where $\text{Li}_x\text{V}_3\text{O}_8$ was supplied by Institute of Physics, Academia Sinica) were assembled and their characteristic of short circuit discharge was performed by recording discharge current at different time intervals.

RESULTS AND DISCUSSION

1. Composition dependence of conductivity

Previous publications indicate that the dissolved salts influence conductivity in

two main manners. On the one hand, the dissociation of salts increases the number of carrier ions and hence enhances ionic conductivity. On the other hand, the micro-viscosity of conduction host is increased by crosslinking like chelating of metal ion with ether oxygen atoms. The mutual compensation of these two factors determines one highest conductivity at a particular salt content range. The conductivities of $\text{PMEO}_{16}/\text{LTS}$ and $\text{PMEO}_{16}/\text{LTBS}$ with different salt content, as shown in Fig.1, reflect a general phenomenon of the PSEs. If comparing the conductivity of two complexes with each other, an interesting difference in the composition dependence of conductivities can be observed. Over the whole salt content range here studied the former ($\text{PMEO}_{16}/\text{LTS}$) demonstrates a little higher conductivity than the latter ($\text{PMEO}_{16}/\text{LTBS}$), but the salt content corresponding to the conductivity maximum is relatively lower (i.e., a greater O/Li value). Unlike general cases, this phenomenon seems not to be interpreted by DSC data since DSC analysis gives close T_g values for these two complexes with the same salt content, implying a similar segmental motion of the polymer hosts. Furthermore, it is difficultly expounded by Lewis acid-base theory since it infers a contrary conclusion. According to this theory toluene-bisulfonic acid should present stronger acidity than p-toluenesulfonic acid due to the electron-attractive property between two sulfonic acid groups of aromatic ring. For this reason, lithium salt of the former should be easily dissociated in solid polyether medium, which therefore affords much more of carrier ions responsible for ion conduction. The contradiction between fact and theoretical speculation may be explained by the difference in the anionic mobility of the complex systems above, which is in fact associated with the anion-cation-dipole interaction. In $\text{PMEO}_{16}/\text{LTBS}$ system the first lithium ion is easier to be dissociated, but the second lithium ion is rather difficult to be done since the second lithium ion not only chelates ether oxygen atoms of PMEO_{16} by cation-dipole interaction but also attracts monovalent anions of LTBS i.e. the bisulfonic anion after the first-grade dissociation by electrostatic force. As a result, the anion-cation-dipole interaction between monovalent LTBS anions and the side chains of PMEO_{16} hinders anionic mobility, and then slows down the total conductivity.

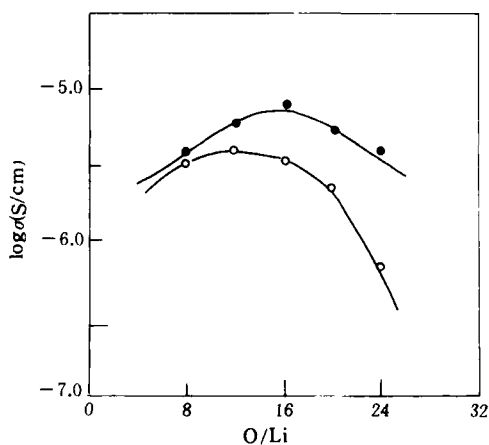


Fig.1 Isothermal conductivity as a function of the composition of the complex at 25 °C
 —●— $\text{PMEO}_{16}/\text{LTS}$; —○— $\text{PMEO}_{16}/\text{LTBS}$

2. Relationship between temperature and conductivity

It has been observed from Fig.1 that the conductivity of the $\text{PMEO}_{16}/\text{LTS}$ and $\text{PMEO}_{16}/\text{LTBS}$ displays a maximum value as O/Li value is located at ca.16 and ca.12 respectively. The temperature dependence of conductivities for these complexes, therefore, are chosen to analyze the factors affecting conductivity as

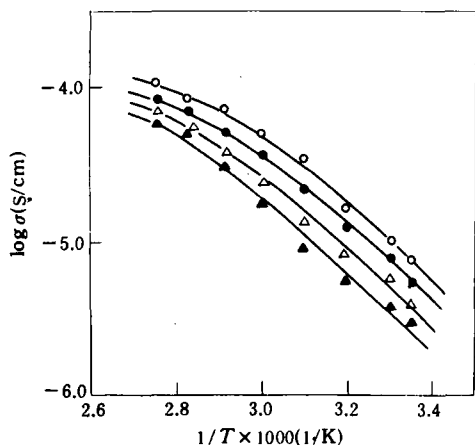


Fig.2 Temperature dependence of conductivities for the complexes

Circle: PMEO₁₆/LTS,

Triangle: PMEO₁₆/LTBS

O/Li=12 (Δ, ●); 16 (▲, ○)

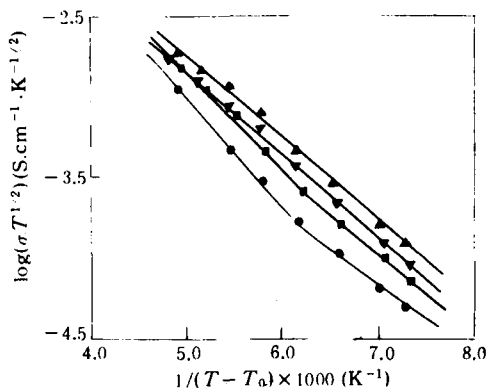


Fig.3 The comparison of VTF plots of the complexes

LTS: O/Li=12 (▼); 16 (▲);

LTBS: O/Li=12 (■); 16 (●)

shown in Fig. 2. Over the whole temperature range the PMEO₁₆/LTS always exhibits higher conductivity than PMEO₁₆/LTBS although the latter closes gradually to the former at elevated temperature. The reason may be attributed to the differences in anionic mobility and in temperature-dependence of the dissociation degree of the added salts rather than in the T_g of the complexes due to their similar T_g values. At lower temperature the conductivity of PMEO₁₆/LTBS is relatively lower since monovalent anions in LTBS are partially fixed in the side chains of PMEO₁₆ by the anion-cation-dipole interaction. As ambient temperature rises, the dissociation degree of LTBS increases much more than that of LTS due probably to further dissociation of the second lithium ion, which increases carrier ions and then enhances conductivity. The DSC curve shows no endothermic peak of oligo (oxyethylene) crystals of PMEO₁₆ over the range of 30 ~ 40 °C, suggesting PMEO₁₆ an amorphous structure desirable for ion transport. This result might be somewhat connected with the crosslinking of polymer chains during film-forming of the complexes by in situ thermal polymerization. The plots of logarithm conductivities against the reciprocal temperature are curved lines, a non-Arrhenius behavior. This fact implies that conductivity is considerably influenced by segmental motion of the amorphous polymer matrix. Thus the Vogen-Tammann-Fulcher (VTF) empirical equation, which describes mass transport properties in amorphous matrix, is used to analyze the conductivity data^[8-10]:

$$\sigma = AT^{-1/2} \exp \left(- \frac{B}{T - T_0} \right)$$

where A , B are constants, T is absolute temperature and T_0 is a temperature related to the T_g . According to Gibbs configurational entropy model the T_0 is regarded as the temperature, below which the configurational entropy is not decreased any more if further dropping of the ambient temperature and is predicted

to be 50 K lower than the T_g [11]. The VTF plots of the complexes obtained by using computer regression (see Fig.3) reveal a difference between two types of complexes. From obtained VTF plots the $(T_g - T_0)$ values of ca. 60K are calculated for these complexes, which all are comparable to what Gibbs theory predicts. It has been known that a linear VTF plot reflects a close correlation of conductivities with the segmental motion in the amorphous polymers. From Fig. 3 two straight lines with different slopes are found for the $\text{PMEO}_{16}/\text{LTBS}$ system, suggesting that there still are other factors to control the ion transport of the complexes besides segmental motion. This may be due to the increase in carrier ions raising from the elevated temperature, which changes the constants of VTF equation. The identification is, however, beyond the scope of the current work. The above phenomena reveal that ionic conductivity of the $\text{PMEO}_{16}/\text{LTBS}$ is influenced not only by segmental motion but also by complicated dissociation of the salts.

3. Discharge characteristic of batteries

So far some techniques have been developed to evaluate Li^+ -ionic transport number (t_+) of the PSEs, none of which is however satisfactory due mainly to the lithium/electrolyte interfacial problems such as passivation growth and dendrite formation. Consequently it is difficult to obtain the consistent t_+ results by different methods even in the same sample, thus the qualitative methods such as dc-polarization and discharge behavior are frequently used to compare the differences in cationic transport number [12]. In the present work the short circuit discharge characteristics of the batteries composed of (Li/complex films/ $\text{Li}_x\text{V}_3\text{O}_8$) as illustrated in Fig.4 are preferably chosen to analyze Li^+ -ionic conduction since it can more effectively distinguish the properties of electrolytes. At initial period the short circuit current (J_{sc}) of the battery containing LTS is greater but rapidly drops to much lower value, showing a poor discharge behavior. On the contrary, the battery with LTBS as the carrier source of the electrolyte supplies a little more stable J_{sc} despite of lower initial current. After 30 min the J_{sc} of both batteries nearly reaches a constant of ca. $60 \mu\text{A}/\text{cm}^2$ respectively, which will remain more than 2h. The fact suggests that there is a difference in Li^+ -ionic transport number between these two complexes, supporting the speculation that the partially-dissociated anions of LTBS may immobilize itself by the anion-cation-dipole interaction. It can be reasonably considered that at lower temperature cationic transport number has been greatly improved by means of increasing negative charge number of the added salts.

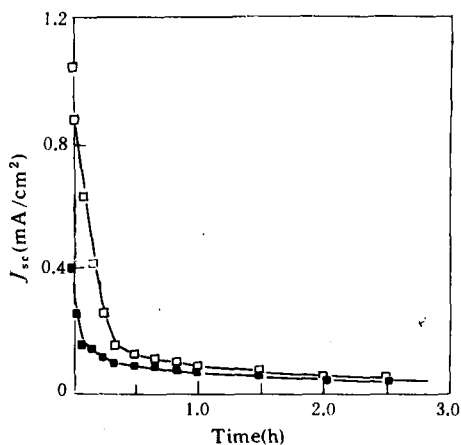


Fig.4 Time dependence of short circuit current in the battery of Li/sample film/ $\text{Li}_x\text{V}_3\text{O}_8$ at 25°C . Film thickness: $100\mu\text{m}$
 —□— $\text{PMEO}_{16}/\text{LTS}$ O/Li = 16;
 —■— $\text{PMEO}_{16}/\text{LTBS}$ O/Li = 12

The above-discussed results have implied us an available approach towards optimizing cationic transport by increasing simply negative charge number of the component salts. It is, of course, also necessary to confirm whether $\text{PMEO}_{16}/\text{LTBS}$ can keep a good cationic transport feature at elevated temperature and to develop polyethers with inflexible backbone required for high conductivity.

Keywords :

Polymeric solid electrolyte ; Ionic conductivity ; Comb-shaped polyether ; Lithium battery

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