PREPARATION AND CHARACTERISTICS OF NOVEL HYPERBRANCHED PEU-BASED GEL POLYMER ELECTROLYTES

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ABSTRACT

Gel polymer electrolytes (GPEs) based on hyperbranched poly (ether urethane) (PHEU) were prepared from the reaction of the hyperbranched polyether (PHEMO) with different diisocyanates in liquid electrolyte. The ionic conductivities and transference number of the GPEs were investigated by alternating current (AC) impedance and multi-potential steps. It is found that the ionic conductivities of GPEs were influenced by diisocyanate structure, lithium salt concentration and addition amount of liquid electrolyte. Sample PUM-0.5M-80% originated from 4, 4-diphenylmethane diisocyanate (MDI) as the hard segment shows the highest ionic conductivity of $2.41 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at ambient temperature. The lithium ion transference number is 0.7. In addition, small molecules of liquid electrolyte were perfectly entrapped by polymer matrix, and liquid leakage in lithium ion battery was avoided.

Keywords: Hyperbranched PEU; GPE; Ionic conductivity; lithium ion battery

INTRODUCTION

GPEs are paid more and more attentions to because of their applications to lithium ion batteries in recent years¹. However, for the conventional poly (ethylene oxide) (PEO)-LiX polymer electrolyte, the significant drawback is the low conductivity at ambient temperature, which is due to high crystallization and poor motion performance of polymer host²⁻⁴. Therefore, there is a continuous challenge to search for a novel polymer electrolyte with high ionic conductivity.

Poly (ether urethane) (PEU) has a two-phase microstructure, where the hard segment domains are distributed in a soft segment matrix⁵. The hard segment provides good mechanical strength, while the soft segment improves the ionic conductivity. The rubbery soft segments can dissolve alkali metal salts, and help achieving high ion mobility, which originates from the interaction of the ether oxygen with the alkali metal ions. In the previous report⁶, the hyperbranched polyether (PHEMO) without stiff groups is selected as soft segment, as well as its amorphous state inherently derived from the hyperbranched molecular structure. Therefore, PHEMO is expected to improve the ionic conductivity of polymer electrolyte⁷. Due to their good mechanical properties, diisocyanates are chosen to act as hard segment domains contributing to the dimensional stability of the polymer electrolytes⁸.

In this paper, GPEs based on PHEU were prepared with hyperbranched polyether (PHEMO) and diisocyanates in liquid electrolyte. Diisocyanates with different structures, such as aliphatic isocyanates of hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI), or aromatic isocyanates of 4, 4-diphenylmethane diisocyanate (MDI) and 2, 4-toluene diisocyanate (TDI) were served as hard segments, respectively. The effects of diisocyanate structure, lithium salt concentration and addition amount of electrolyte on the ionic conductivities of the as-prepared GPEs were discussed and compared.

EXPERIMENTAL

Materials

Lithium trifluoromethanesulfonimide (LiTFSI) was purchased from Aldrich. The other reagents used to synthesize PHEMO were described in our previous work¹⁶. The diisocyanate, i.e., HDI, MDI, IPDI, and TDI were kindly provided by Liming Institute of Chemical Industries, China. Triethylene glycol dimethyl ether (TGE) and dibutyltin dilaurate (T-12) were purchased from Acros.

Preparation of GPE

The synthesis of PHEMO has been described previously^{6,9}. A series of TGE-dissolved LiTFSI with various concentrations from 0.1 to 3.0 mol/L were prepared, and used as the liquid electrolytes. Different amount of PHEMO was mixed with diisocyanate in the liquid electrolyte, and then T-12 catalyst was added. This reaction was carried out in a nitrogen-flushed oven at 50 °C for 24 hrs to obtain a PHEU gel polymer electrolyte. Different GPEs were obtained by using various diisocyanates. Fig.1(a) shows the scheme of the preparation of PHEU, and the structures of HDI, MDI, IPDI and TDI are shown in Fig.1(b).

Fig.1 Scheme of the preparation of PHEU by the reaction of PHEMO and MDI (a); the structure of HDI, MDI, IPDI and TDI (b)

Composition of GPE

In this study, PUH, PUM, PUI and PUT represent the as-prepared GPEs, where the hard segments of the polymer matrix are HDI, MDI, IPDI and TDI, respectively. PUH-1M-50% means the GPE with the hard segment of HDI, the lithium salt concentration of 1mol/L and the addition amount of liquid electrolyte of 50% (50% refers to the mass ratio of the liquid electrolyte to the polymer matrix).

Electrochemical measurements

The ion conductivities were evaluated from A.C. impedance technique over a frequency range $1 \times 10^5 \text{ Hz}$ using CHI 660A electrochemistry workstation (Shanghai Chenhua Instrument Co. Ltd.). The measurements were carried out from 30 to 80 °C with an interval of 10 °C.

Lithium ion transference number, t_{Li^+} , was tested using the method of multi-potential steps, which was calculated using the following equation: $t_{\text{Li}^+} = I_{\text{ss}} / I_0$, where I_0 and I_{ss} are the initial and steady-state currents, respectively¹⁰. A well sealed symmetrical Li/GPE/Li experimental cell was assembled in a glove box and tested using CHI 660A electrochemistry workstation to determine the transference number t_{Li^+} .

RESULTS AND DISCUSSION

Ionic conductivities

The ionic conductivities of the as-prepared GPEs have a tendency to increase with the increasing temperature, following the Arrhenius equation¹¹, as shown in Fig.2. With increasing temperature, the mobility of polymer chains

is enhanced, and the fraction of free volume in the polymer matrix increases. Therefore, high ionic conductivity can be achieved. With the same lithium salt concentration and the same electrolyte adding amount, PUH and PUM with straight chain deliver higher ionic conductivities than PUI and PUT with ring structure, because straight chains can achieve excellent flexibility and mobility^{12, 13}

Fig. 2 Dependence of ionic conductivities on different diisocyanates

Fig.3 shows the dependence of the ionic conductivities on different lithium salt concentration. Four curves show a trend of increase at first, and then decrease. It is observed that when the lithium salt concentration is 1mol/L, PUH and PUM have the highest conductivities at ambient temperature, whereas PUI and PUT have the highest conductivities with 2mol/L lithium salt. It is well known that the amount of lithium ion plays an important role on the ion conductive process. With increasing lithium salt concentration, the amount of free transfer lithium ion increases correspondingly, therefore leads to an ionic conductivity enhancement. However, when increasing lithium salt concentration to some degree, formation of transient cross-link between lithium ion and the ether group can decrease the segmental motion of the polymer chain¹⁴, which results in a decrease in the mobility of the charge carrier.

Fig. 3 Dependence of ionic conductivities on different lithium salt concentrations

Fig. 4 shows the relationship between the conductivities of the GPEs and the adding amounts of the liquid electrolytes. When the lithium salt concentration remains constant, the ionic conductivities of PUH, PUM, PUI

and PUT strongly increase with the increasing addition amount of the liquid electrolyte. As we known, the ionic conductivity is mainly dependent on the diffusion rate and the amount of lithium ion. Therefore, the more the adding amount of the liquid electrolyte is, the more the content of lithium ion is. The GPE is composed of polymer matrix containing the liquid electrolyte, which is similar to a stuffing enclosed with a piece of dumpling wrapper. If there is too much stuffing, the dumpling wrapper may be broken. Namely, if the addition amount of the liquid electrolyte is too much to be involved in the polymer matrix, the GPE fails to form a free-standing membrane. Therefore, in this study, the maximum adding amount of liquid electrolyte for PUH, PUI and PUT is proved to be 67wt%, whereas that for PUM is 80wt%. It can be found that when the lithium salt concentration is 0.5mol/L and the GPE containing 67wt% liquid electrolyte, the conductivities of PUH, PUM, PUI and PUT are $3.52 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$, $4.25 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$, $4.74 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$, $2.59 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at ambient temperature, respectively. Moreover, it is clear that the ionic conductivity of PUM-0.5M-80% containing 80wt% liquid electrolyte is the highest, $2.41 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ at ambient temperature, as shown in Fig.4(b). Because the hard segment of MDI has a straight chain with two phenyls, PUM exhibits better mechanical properties than the other GPEs do¹⁵, therefore it can entrap more liquid electrolytes, and result in the highest ionic conductivity.

Fig. 4 Dependence of ionic conductivities on the adding amount of the liquid electrolytes.

Lithium ion transference number

Lithium ion transference number, t_{Li^+} , which is one of the most important parameters for lithium ion batteries, was evaluated using multi-potential steps technique. A relative high t_{Li^+} can eliminate the concentration gradients in the battery and ensure its operation at high current density. All parameters used for the calculation of t_{Li^+} can be obtained directly from the current response of the Li/GPE/Li experimental cell. In the system of PUM-0.5M-80% GPE, lithium ion transference number is as high as 0.7, as shown in Fig.5.

Fig.5 Multi-potential steps curves of PUM-0.5M-80% GPE

CONCLUSIONS

A novel type of hyperbranched gel polymer electrolytes is prepared by PHEMO and different diisocyanates. Ionic conductivities of the as-prepared gel polymer electrolytes increase at first, and then decrease with the increasing lithium salt concentrations. The amount and mobility of the lithium ion can be enhanced by increasing the adding amount of the liquid electrolyte. The highest ionic conductivity is $2.41 \times 10^{-3} \text{ S cm}^{-1}$ (sample PUM-0.5M-80%) at ambient temperature, because PUM with the MDI consisting of a chain with two phenyls, therefore this GPE has better mechanical properties and can entrap more liquid electrolytes. In addition, the small molecules of the liquid electrolyte were perfectly enwrapped by the polymer matrix, thus help avoiding the electrolyte leakage, and enhancing the safety of lithium ion battery.

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