AENSI Journals

Australian Journal of Basic and Applied Sciences

ISSN:1991-8178

Journal home page: www.ajbasweb.com

Lithium Polymer Battery Based on Cross-linked Polymer Electrolyte

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ARTICLE INFO

Article history:
Received 20 November 2013
Received in revised form 24 January 2014
Accepted 29 January 2014
Available online 5 April 2014

Keywords:

ABSTRACT

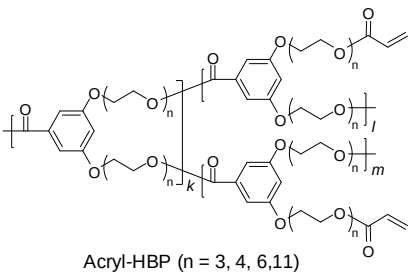
Cross-linked solid polymer electrolytes composed of oligomeric PEO, Acryl-HBP having various ethylene oxide (EO) chain length and $LiN(SO_2CF_3)_2$ were prepared, and the effects of molecular weight of PEO, ethylene oxide (EO) chain length in the Acryl-HBP, and cross-linking methods such as radical initiation and electron beam (EB) irradiation upon the ionic conductivity and mechanical property were investigated. And also $Li_4Ti_5O_{12}$/cross-linked solid polymer electrolyte/$LiFePO_4$ cell was assembled and cell performace was evaluated.

To Cite This Article: I. Takahito, S. Takahiro, K. Mitsuru, M. Masashi, U. Takahiro Uno, K. Masataka, H. Kazuma, I. Nobuyuki, T. Yasuo.., Lithium Polymer Battery Based on Cross-linked Polymer Electrolyte. ***Aust. J. Basic & Appl. Sci.,*** *8(4): 405-408, 2014*

INTRODUCTION

Complexes of poly(ethylene oxide) (PEO) with lithium salts are known as a typical example of ion conductive materials, and their applications to solid polymer electrolyte (SPE) for all solid-state rechargeable lithium batteries have been studied extensively (MacCallum, J. R. and Vincent, C. A., 1987 and 1989; Scrosati, B. and R. J. Neat, R. J., 1993; Bruce, P. G., 1995; Gray, F. M., 1997). However, they have disadvantages of low ionic conductivity at room temperature. It is desirable for solid polymer electrolytes to show ionic conductivity like conventional organic liquid electrolytes and mechanical properties that are able to separate the electrodes. We have investigated SPE composed of hyperbranched polymer with acetyl groups at the periphery (Ac-HBP), high molecular weight PEO, and $LiN(SO_2CF_3)_2$ (LiTFSI) (Wen, Z. *et al*., 2000). The SPE showed high ionic conductivity over the wide temperature range. Replacement of Ac-HBP with cross-linkable HBP (Acryl-HBP), which has acryl groups at the periphery of HBP, improved the mechanical property of the SPE though the ionic conductivity decreased (Itoh, T. *et al*., 2005).

In this work, the cross-linked solid polymer electrolytes composed of oligomeric PEO, Acryl-HBP having various ethylene oxide (EO) chain length and LiTFSI were prepared by using radical initiator and electron beam (EB) irradiation, and the effects of molecular weight of PEO, ethylene oxide (EO) chain length in the Acryl-HBP, and cross-linking methods on their ionic conductivity and mechanical property and also application of the cross-linked SPE to polymer battery were investigated.



Acryl-HBP (n = 3, 4, 6,11)

Oligomeric PEOs (M_n = 222, 300, 500, 1000, and 2000, Aldrich) and benzoyl peroxide (BPO, Wako Chemicals) were used without further purification. Copolymer of ethylene oxide and allyl glycidyl ether (EO-AGE) was kindly supplied by Meisei Chemical Works LTD. LiTFSI (Fluka) was dried under vacuum at 120 ^oC prior to use and kept inside an argon-filled glove box.

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Experimental:

Materials:

Acryl-HBPs with various EO chain length (Acryl-HBP (n = 3, 4, 6, 11)), the chemical structure of which is shown below, were prepared according to the procedure reported previously (Itoh, T., Gotoh, S., Uno, T., Kubo, M., 2007).

Preparation of cross-linked solid polymer electrolyte:

All preparation procedures were carried out inside a dry argon-filled glove box. Given amounts of oligomeric PEO, Acryl-HBP, BPO if necessary, and LiTFSI were dissolved in acetonitrile, and vigorously stirred for 12 h. The resulting solution was poured onto a terephthalimide film, and acetonitrile was evaporated very slowly at room temperature to prepare a casting film. In the case of radical initiation using BPO, the casting film was dried and cross-linked by heating at 90 °C for 24 h. The cross-linked SPE films were peeled from the terephthalimide film and stored inside the glove box. In the case of EB irradiation, the casting film was cross-linked by EB irradiation with 12 Mrad for 10 second at room temperature in a nitrogen atmosphere.

Cross-linked SPE for cell performance test was prepared by the EB irradiation on the casing film composed of PEO with molecular weight of 500, Acryl-HBP (n=4) with 4EO, EO-AGE as a modifier of cross-linking density, and LiTFSI (Li/O = 1/12).

Measurements:

The ionic conductivities of the cross-linked solid polymer electrolytes were measured by a two-probe method after the samples were fixed inside a Teflon Oring spacer with known thickness and sandwiched between two stainless steel (SS) electrode disks acting as ion-blocking electrodes and set in a thermostat oven chamber. The measurements were carried out using a Solartron 1260 impedance/gain-phase analyzer over a frequency range of 10^6 to 1 Hz and a temperature range of 80 to −10 °C with an amplitude of 10 mV. All samples were first kept at 80 °C for at least 12 h and then measured during the cooling cycle. The measurements were carried out after keeping the samples at each temperature for 1 h to attain thermal equilibration. The data were processed by using an appropriate fitting program.

Charge-discharge performance was measured galvanostatically at 40 ^oC with a C/10 rate using a charge-discharge measurement system. The carbon-coated $LiFePO_4$ ($LiFePO_4$/C) was used as the cathode active material, and vapor grown carbon fiber (VGCF, Showa Denko) as a conductive agent. $Li_4Ti_5O_{12}$ (LTO, Ishihara Sangyo LTD) was used as the anode active material. The weight ratio of $LiFePO_4$/C: VGCF: SPE was 44: 11: 45 and that of LTO/VGCF/SPE was 45: 5: 50, respectively. A mixture of the componet in acetonitrile was cast on Al foil for the cathode electrode and on Cu sheet for the anode electrode with an applicator. The film was cross-linked by EB irradiation at a dose of 270 kGy in a nitrogen atomosphere at an accelarating voltage of 220 kV. The $LiFePO_4$/C/SPE/Li half cell and LTO/SPE/Li half cell were constracted.

RESULT AND DISCUSSION

Effects of PEO molecular weights and cross-linking method on ionic conductictivity:

Temperature dependence of the ionic conductivities for the cross-linked $[80\%PEO/20\%Acryl\text{-}HBP]_{12}$(LiTFSI) electrolytes using PEO with various molecular weights, and Acryl-HBP (M_n=4500) is shown in Fig.1, where Fig.1a and Fig.1b correspond to the cross-linked SPE prepared by BPO initiation and EB irradiation methods, respectively. The polymer electrolytes containing lower molecular weights PEO with showed better ionic conductivities compared with those containing higher molecular weights PEO in both preparation methods. However, the polymer electrolytes obtained by the EB irradiation method showed much better ionic conductivity than those obtained by BPO initiation one. Moreover, the EB irradiation method (10 sec) has an advantage in the point of reaction time view to prepare the ross-linked SPE in comparion with the BPO initiation method (24 hs).

The polymer electrolytes containing PEO of M_n=500 showed thermal stability of 250^{o}C at 5wt% weight loss and the flash point of over 250^{o}C, indicating that they have good safety of battery application.

Effect of EO chain length of Acryl-HBP on ionic conductivity:

The ionic conductivities of the cross-linked $[80\%PEO/\ 20\%Acryl\text{-}HBP]_{12}(LiN(SO_2CF_3)_2)$ electrolytes using PEO of M_n=500 and Acryl-HBP having different chain length (3EO, 4EO, 6EO, and 11EO) obtained by BPO initiation at -10, 20, 50, and 80 ^oC are shown in Fig.2.

The polymer electrolytes using Acryl-HBP with 11EO units showed a little bit lower ionic conductivity compared with those having shorter chain length (3EO, 4EO, and 6EO). Polymer electrolyte having Acryl-HBP with a chain length of 4EO showed the relatively higher ionic conductivity among these four polymer electrolytes. Therefore, Acryl-HBP with a chain length of 4EO was chosed as a component of cross-linked SPE for the cell performance mentioned later. And also, all of polymer electrolytes exhibited almost same Tg values

and decomposition temperatures. This indicates that the change of the EO chain length does not affect significantly thermal properties of the polymer electrolytes.

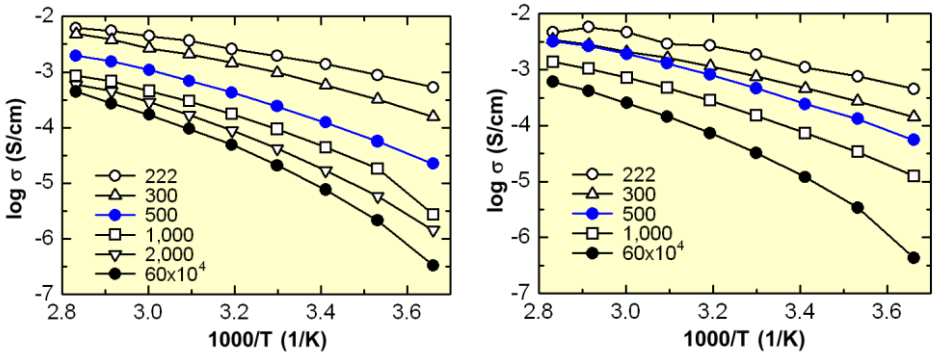

Fig. 1: Temperature dependences of the ionic conductivities for the cross-linked polymer electrolytes of Acryl-HBP, PEO with various molecular weight, and LiTFSI prepared by (a) radical initiation method and by (b) EB irradiation method.

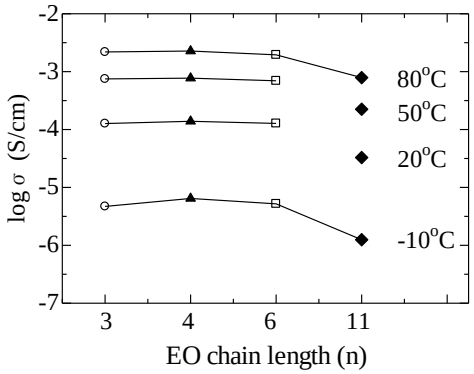

Fig. 2: The relationship of the ionic conductivities at various temperatures such as -10, 20, 50, and 80 ^{o}C and the EO chain length.

Cell performance:

To demonstrate the applicability of the cross-linked SPE in lithium cells, the charge-discharge perfromances of the $LiFePO_4$/cross-linked SPE/Li and of the LTO/cross-linked SPE/Li were tested. The charge-discharge curves for the $LiFePO_4$/Cross-linked SPE/Li cell and for the LTO/Cross-linked SPE/Li cell at 40 ^{o}C with C/10 rate are shown in Fig. 3a and Fig. 3b, respectively.

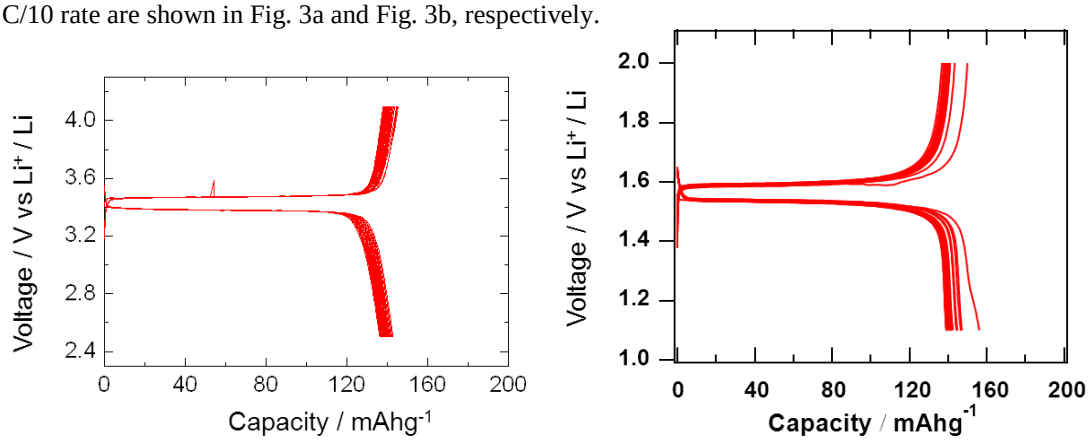

Fig. 3: Typical charge/discharge profiles for (a) the $LiFePO_4$/cross-linked SPE/Li cell and (b) for the LTO/cross-linked SPE/Li cell at 40 ^{o}C and with C/10 rate.

A capacity of aproximately 140 mAh/g was obtained for the cross-linked SPE in both half-cells. The cyclying properties indicated good cyclability for the cell with the cross-linked SPE with an average columbic efficiency of 96% at the second cycle and of 95% at the 20 cycles.

The Cu/LTO/cross-linked SPE/$LiFePO_4$/Al cell was assembled to test the capacity of the electrolyte to perform in a real battery configuration. Initial voltage profiles of the lithium polymer battery cycled at 25 ^oC and at low C/10 rate is shown in Fig. 4. The initial capacity was of the order of 42 mAh/g. The cell operating voltage was around 1.8 V vs Li/Li+, reflecting the electrochemical process of lithium cycling transfer from cathode to the anode. As from the figure, the charge and discharge plateaus are well defined. Overall, a charge/discharge efficiency approaching 99% and a capacity of the order of 42 mAh/g were obtained after 100 cycles and even after 200 cycles for the Li-ion cell.

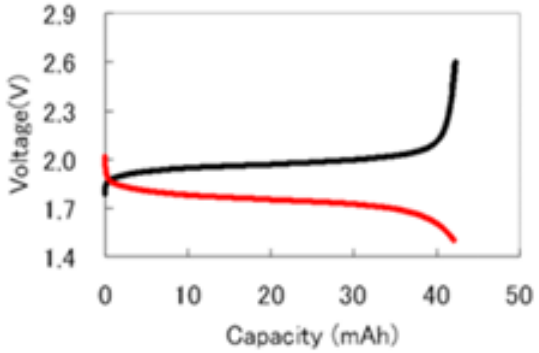

Fig. 4: Typical initial charge/discharge profile of the LTO/cross-linked SPE/$LiFePO_4$ cell cycled between 1.5 and 2.6 V at 25 ^oC and at C/10 rate.

Conclusions:

Ionic coductivity of the cross-linked SPE increased with an increase of molecular weight of PEO. The difference of the EO chain length in Acryl-HBP showed no significant effect on the ionic conductivity. EB irradiation was better method to prepare cross-linked SPE than radical initiation and in the point of reaction time view. Ionic conductivity, thermal stability, and mechanical strength were acceptable for cell application. Good cell performance was observed in the lithium-ion cell using the cross-linked SPE.

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