Ionic Conductivity of New Thermally Stable Polymer Electrolyte for Lithium-Ion Batteries

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Introduction

In order to obtain a high performance polymer electrolyte for lithium-ion batteries, a number of studies have been conducted [1,2]. The characteristics of the polymer electrolyte, especially thermal stability, mechanical strength and no liquid-leak, are essential advantages for designing the batteries for electric vehicles. Since such kind of batteries using the polymer electrolyte is ordinary used around at 60-80°C for at least 5 years, the thermal stability and mechanical strength of the polymer electrolyte at high temperature are strongly demanded. In this paper, we will propose a new thermally stable polymer electrolyte, that was prepared by co-polymerization of bis-phenol A dimethacrylate modified with ethyleneoxide (EO) (PDBE450) as a thermally and mechanically stable matrix monomer, and poly-(ethyleneglycol) (PEG)-monomethacrylate (PME400) as a EO side chain monomer to give rise to high ionic conductivity and flexibility.

Experimental

Polymer electrolyte films were prepared by mixing PDBE450, PME400 (Fig.1, supplied from NOF) and bis-trifluoromethanesulfonimide (LiTFSI, Fluka) as a lithium salt, pouring the mixture into Teflon pool and radical polymerization with azobisisobutyronitrile (AIBN), where the molar ratio of PDBE450/PME400 and the concentration of Li salt were changed. The ionic conductivity of the electrolyte film was measured by the AC impedance technique using a computer controlled Hewlett-Packard 4192A LF impedance analyzer. The thermal stability of the electrolyte was investigated by thermogravimetry (TG) using TGD-9600 (Shinku-riko).

Results and discussion

In order to obtain an electrolyte having a higher ionic conductivity, the molar ratio of PDBE450 / PME400 was changed and the temperature dependence of the ionic conductivity for the each sample was measured (Fig.2). The ionic conductivity of the electrolyte was gradually increased at all ranges of the measuring temperature as increasing the amount of PME400. It indicates that the mobility of the Li-ion carrier in the electrolyte was accelerated by the increase of the EO side chain, just like a comb-type polymer electrolyte[3]. Fig.3 shows TG curves of those samples. Up to the molar ratio of PDBE450/PME400=1/ 6, the decomposition temperature was not changed. The electrolytes were thermally stable up to near 300°C. But the thermal stability was declined above the molar ratio=1/7 and new thermal de-composition peak appeared around 400°C. Therefore we concluded that the composition of PDBE450/PME400 = 1/6 at the molar ratio is optimum for the polymer electrolyte film formation. Furthermore, on the sample of the molar ratio=1/6, Li salt concentration was changed and the influence on the ionic conductivity for those samples was investigated. The highest conductivity was found for the sample with Li salt concentration of 1/16 (molar ratio: Li^+/ EO), the value of the ionic conductivity was 2.7 x 10^{-4} S cm^{-1} at 80°C and 9.7 x 10^{-5} S cm^{-1} at 60°C, respectively. We will also report on the sample prepared with diacrylate-type bis-phenol A (ADBE450).

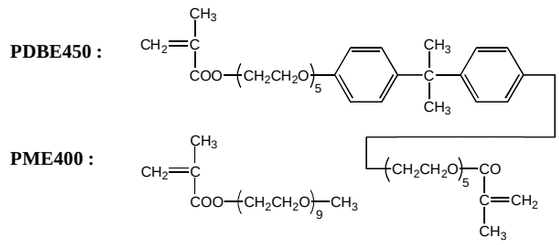

Fig. 1 Structure of PDBE450 and PME400.

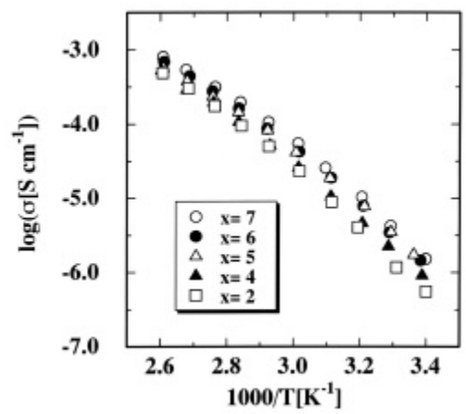

Fig. 2 Arrhenius plots of ionic conductivity for PDBE450 / PME400 (molar ratio: 1/ x) + LiTFSI (Li^+/EO= 1/ 8).

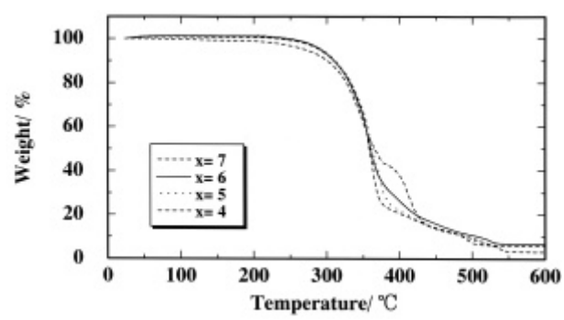

Fig. 3 TG curves of PDBE450/PME400 (molar ratio: 1/x) + LiTFSI (Li^+/EO= 1/ 8). Heating rate: 5°C /min.

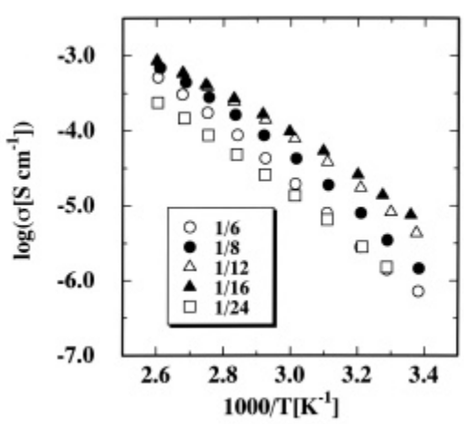

Fig. 4 Arrhenius plots of ionic conductivity for PDBE450 / PME400 (molar ratio: 1/ 6) + LiTFSI (Li^+/EO= 1/ x).

References

[1] J.R. MacCallum, et al, Polymer Electrolyte Reviews 1 and 2, Elsevier (1987, 1989); [2] B. Scrosati, Applications of Electroactive Polymers (1993); [3] A. Nishimoto, et al, Electrochimica Acta, 43 (1998) 1177.