Synthesis of Novel Nano-Structure-Controlled Solid Polymer Electrolyte and its Battery Characteristics

Takeshi Niitani*, Mikiya Shimada*, Masato Amaike*, Kiyoshi Kawamura*, Kiyoshi Kanamura** *Nippon Soda Co., Ltd. 12-54 Goi Minamikaigan, Ichihara, Chiba 290-0045 Japan **Tokyo Metropolitan University

1-1 Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan

Introduction

Both high ionic conductivity and high mechanical properties are required to the solid polymer electrolyte for all of the solid lithium-polymer batteries. To satisfy these requirements, we have synthesized two kinds of block copolymers using a living radical polymerization technique. Fig.1 shows the structure of the BAB-block copolymer (MES-polymer) and the CBABC-block copolymer (MESH-polymer). A novel nano-structure controlled solid polymer electrolyte (SPE) consists of polystyrene (PSt) block to improve the mechanical properties and polyethyleneoxide (PEO) moiety to provide the ionic conductivity.

Experimental

MES- and MESH-polymers were synthesized by the living radical polymerization technique as shown in Fig.1. In the first step, methoxypolyethyleneglycol monomethylmethacrylate was polymerized with ruthenium(II) complexes. The obtained polymer was used as a macroinitiator for block copolymerization with styrene MES-polymer). The MESH-polymer was synthesized by the successive block copolymerization with hydroxyethyl acrylate (HEA).

After the isolated copolymer and Li salts were dissolved in THF, the mixture solution was cast on an aluminum plate. The solvent was allowed to evaporate at room temperature in the glove box for overnight and then under high vacuum for 5h at 120° C. The thickness of SPE layer was about 80μ m.

Results and Discussion

Fig.2 shows temperature dependence of ionic conductivity. The ionic conductivity of 1E-4 S/cm at 30 $^{\circ}$ C was obtained in the ratio of [Li]/[EO]=0.05 and the tensile strengths of these films were about 3MPa.

Fig.3 shows TEM image of MES-polymer. The micro phase separation with the continuous phase of PEO forming a network structure was observed. Moreover, when MESH-polymer was crosslinked by Tolylene 2,4-diisocyanate (TDI), TEM image revealed very interesting segregation phenomena (Fig.4).

An all-solid state rechargeable lithium cell of LiCoO2/ SPE/Li was successfully prepared by using MES- and MESH-polymers. The cell performed excellent charge/

discharge character with keeping a discharge capacity of 100mAh/g after 100 cycles at 25 °C. Moreover, this SPE has the stability of 5V (vs Li/Li⁺) at 60 °C.

From the above results, this SPE is expected to the application of a room-temperature-operation-type and high-energy battery.

References

1) T. Niitani, M. Shimada, K. Kawamura, Y.H. Rho, K.Kanamura, *The Electrochemical Society of Japan*, 2B31-2B33 (2003).







Fig.2 Temperature dependence of ionic conductivity



Fig.3 TEM image of MES-polymer



Fig.4 TEM images of MESH-polymer

2) T. Niitani, M. Shimada, K. Kawamura, Y.H. Rho, K.Kanamura, *The 44th Battery Symposium in Japan*, 3D22-3D23 (2003).

3) M. Shimada, T. Niitani, K. Kawamura, K.Kanamura, *The Electrochemical Society of Japan*, 1123 (2004).