Charge-Discharge Electrochemical Properties of Li-Secondary Batteries with Nano-Structure-Controlled Solid Polymer Electrolyte (SPE)

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Introduction

We have reported that BAB (St-b-PME-b-St) blockcopolymer (MES) showed the micro phase separation with the continuous phase of polyethyleneoxide (PEO) forming a network structure and a good charge-discharge behavior.

However, the composite-electrode using MES showed the poor electrochemical repeatability and the low durability of the Li dendrites. We investigated that solid polymer electrolyte using PME-b-St-b-hydroxyethyl acrylate (MESH) crosslinked by urethane bonds employing tolylene 2,4-diisocyanate (TDI) was prepared to improve the electrochemical and mechanical properties. Furthermore, we investigated LiPF6, LiTFSI as Li salt for the practical use.

Experimental

A composite powder consisted of $LiCoO_2$, ketjen black (KB), polyvinylidene fluoride (PVdF) by the weight ratio of 85:7:8 was used as a positive electrode. Li salt ($LiPF_6$ or $LiClO_4$) was added to the MES (PME/St=90/10) and the mixture was dissolved in tetrahydrofuran/acetone. The ratio of Li ion and oxygen atoms of PEO was set 1:20. The solution was cast on the positive electrode to permeate MES and the electrode was heated to remove solvents.

In order to prepare SPE on the composite-electrode, MESH (PME/St/HEA=77/7/16), Li salt, and TDI were dissolved in tetrahydrofuran/acetone and cast on the composite-electrode. The thickness of SPE layer was about 20-30μm.

Coin-type cells (2016) were assembled using counter electrode of metallic lithium and the composite-electrode/SPE. The charge-discharge test was carried out (HJ1010mSM8, Hokuto Denko, Japan) at 60°C at 0.05C rate and the voltage limit was 3.0-4.2V for charge-discharge.

Results and Discussion

Fig.2 shows charge-discharge curves of the $LiCoO_2$/MES/MESH/Li cell using $LiPF_6$. Fig.3 shows the cycling performance on charge-discharge capacities for the $LiCoO_2$/MES/MESH/Li cell using the SPE.

These results indicate;

(1) The MES/MES type cell showed good repeatability of the charge-discharge properties and durability of the Li dendrites.

(2) $LiPF_6$, LiTFSI was effective on the equal level of $LiClO_4$.

(3) In the first discharging process, discharge capacity of about 120 $mAhg^{-1}$ was obtained. The cell performed good charge-discharge properties, keeping a capacity of 100$mAhg^{-1}$ after 50 cycles at 60 ^oC. In the discharging process, a plateau is observed at about 3.85V.

Therefore, MES/MESH crosslinked by urethane bonds are expected to be the SPE for the practical application.

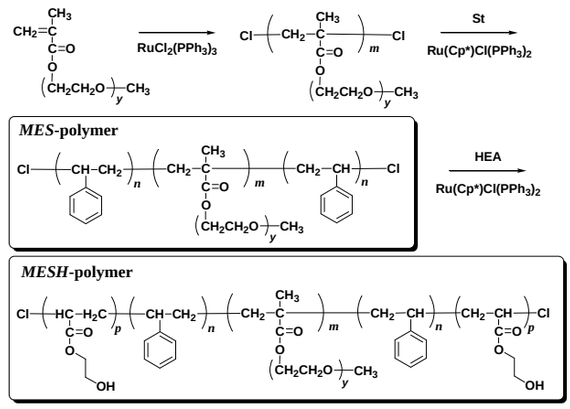

Fig.1 Synthesis of Block copolymers

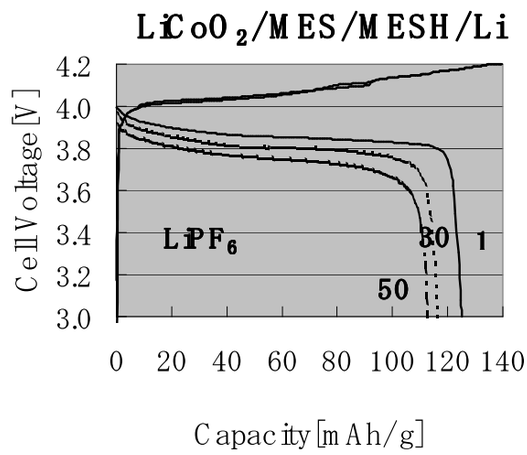

Fig.2 Charge-discharge curves of $LiCoO_2$/MES/MESH/Li cell

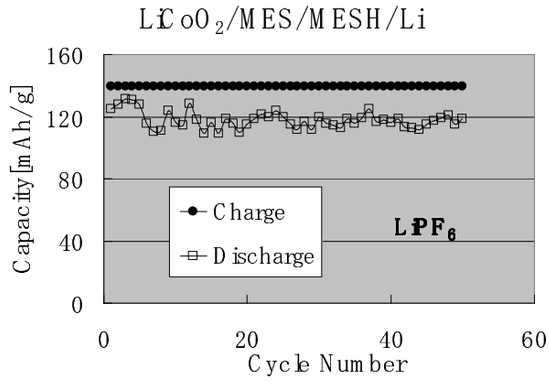

Fig.3 Capacity change of $LiCoO_2$/MES/MESH/Li Cell during the charge-discharge

References

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