

Preparation of Gel Electrolyte using Self-assembling Diblockpolymer for Lithium Secondary Battery

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Introduction

Polymer electrolytes for lithium secondary battery have been studied for several years for safety issues in future Li batteries, and gel polymer electrolyte is one of the most promising candidates at present.

Our group had studied the gel electrolyte prepared by hot-blending of two polymer, polyethylene oxide (PEO) serving ionic conductivity and polystyrene (PS) serving mechanical strength, for lithium secondary battery. This gel electrolyte has micro phase separation structure. Then, constant current charge-discharge test with lithium metal anode. Revealed that to obtain better charge-discharge cycle, retaining large amount of plasticizer in electrolyte was requisite [1]. As the large amount of plasticizer fluidizes PEO, ionic conductive phase, there is possibility that fluidized PEO flows out from PS matrix.

In this study, we aim to make a gel electrolyte which can retain large amount of plasticizer without fluidizing PEO phase. For that purpose, we selected diblockpolymer which is composed by bonding PEO and PS chain end-to-end. The gel electrolyte was made by self-assembling of this diblockpolymer. It is said that the membrane made from this diblockpolymer has micro phase separation structure.

Experimental

For making gel electrolyte, the PEO/PS diblockpolymer ($M_n=8.0 \times 10^4$, PEO content 36 wt %, SOWA SCIENCE CORPORATION) was dissolved in toluene as removal solvent. Liquid electrolyte, LiBF_4 /EC-PC (1:1 vol.), was added to this polymer solution as plasticizer and source of supporting electrolyte. The gel electrolyte was made by casting of this mixture on Cu plate followed by evaporation process of toluene.

In order to confirm micro phase separation structure, Atomic force microscopy (AFM) was carried out. The gel electrolyte for AFM was spin-coated from the mixture on a Cu plate, because the surface of the gel electrolyte made by casting was too rough to observe. Besides the membrane was spin-coated from the solution without adding the plasticizer for comparison.

To measure the ionic conductivity, Cu/gel electrolyte/Ni cell was assembled and the ionic conductivity measurement was carried out by a.c. impedance measurement. The impedance spectrum was measured in the constant potential mode by sweeping the frequencies from 20 kHz to 100 mHz at a.c. amplitude of 500 mV.

To evaluate the chemical stability against oxidation, Li/gel electrolyte/Au cell was assembled. Linear sweep voltammetry (LSV) was carried out about this cell.

Results and discussion

The membrane spin-coated from the solution without adding the plasticizer was observed by AFM. The structure such as dots dispersing regularly on the surface

of this membrane was observed. From this result, it is suggested that this membrane had spotted micro phase separation structure. Aiming ionic conductive phase is expanded by adding the plasticizer to spin-coating solution, the gel electrolyte was prepared. The surface of this gel electrolyte observed by AFM (Fig.1) suggested that the structure of this gel electrolyte had lamella structure. It is considered that this structure change was caused by changing the interaction and volume fraction between PEO and PS phase with adding the plasticizer.

The ionic conductivity of this gel electrolyte was measured. The ionic conductivity of this gel electrolytes prepared by altering the amount of plasticizer and the concentration of lithium salt was in the range between 5.66×10^{-4} and 5.52×10^{-5} S/cm. The precise report about the ionic conductivity made will be given at the presentation.

For evaluation the chemical stability of this gel electrolyte against oxidation, LSV was carried out using Li/gel electrolyte/Au cell. The current derived from oxidation started at 5.5 V vs. Li / Li^+ (Fig.2).

These results suggested that gel electrolyte using self-assembling of diblockpolymer can be one of the candidates of electrolyte for future lithium secondary battery.

Acknowledgement

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Reference

[1] T. Momma, H. Ito, H. Nara, H. Mukaibo, S. Passerini, and T. Osaka, *Electrochemistry*, **71**, 1182 (2003).

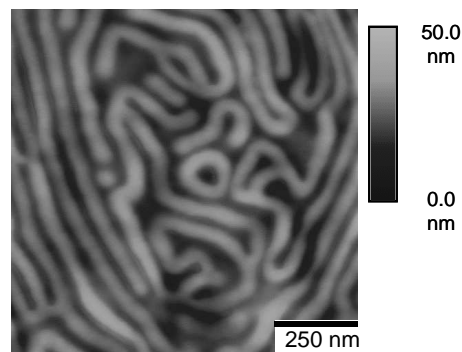


Figure 1. AFM image of the spin-coated gel electrolyte.

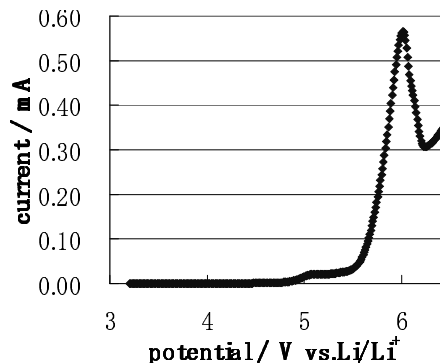


Figure 2. LSV curve of the gel electrolyte.