

***In situ* SEM observation of solid-state lithium polymer batteries**

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Introduction

R&D activities for large format lithium ion batteries (LIB) are getting more attention due to the utilization of the renewable energies and the commercialization of electrical vehicles. However the safety concerns of LIBs still remains, because of the flammable electrolyte solutions. Considering the safety issue of the LIBs, solid-state batteries are one of the possible solutions to improve the battery safety.

Our group has been working on a solid-state battery system using a polyethylene oxide (PEO) based solid-state electrolyte with graphite or silicon based negative electrode[1, 2]. We recently found that the microstructure of the electrode is crucial to obtain the satisfactory cycleability of the cell, because the electrode easily delaminate from the polymer electrolyte / the current collector during the charge-discharge cycles resulting in the immediate capacity fading. We suspect that the volume expansion of the active materials initiates the delamination of the electrode, however it is difficult to prove it just by the *ex-situ* SEM observation of the electrodes before / after the charge-discharge test.

Here we demonstrate an *in situ* SEM observation of the electrode-electrolyte interphase for the all-solid polymer batteries and discussed the mechanism of the capacity fading.

Experimental

The silicon electrode was prepared as follows; 70 wt % of silicon powder (particle size 500nm), 15 wt % of carbon nanofiber (20 μm in length) as conductive additive and 15 wt % of the binder (mixture of styrene butadiene rubber and sodium carboxyl methyl cellulose with 1:2 weight ratio) were mixed in water. The mixtures of the electrode components were casted on a copper foil, and dried at 120 $^{\circ}\text{C}$ under vacuum for 3 h. The polymer electrolyte was prepared by dissolving PEO and $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ ($\text{Li}/\text{O} = 1/18$) into acetonitrile and dried at 110 $^{\circ}\text{C}$ for 10 h under vacuum.

The Silicon electrode was bonded the polymer electrolyte together and heated at 70 $^{\circ}\text{C}$ for 1 h to diffuse the LiTFSI salt from the polymer electrolyte to the silicon electrode.

A specially designed *in situ* SEM cell was fabricated in the argon filled glove box and introduced into the SEM chamber without exposed in the atmosphere.

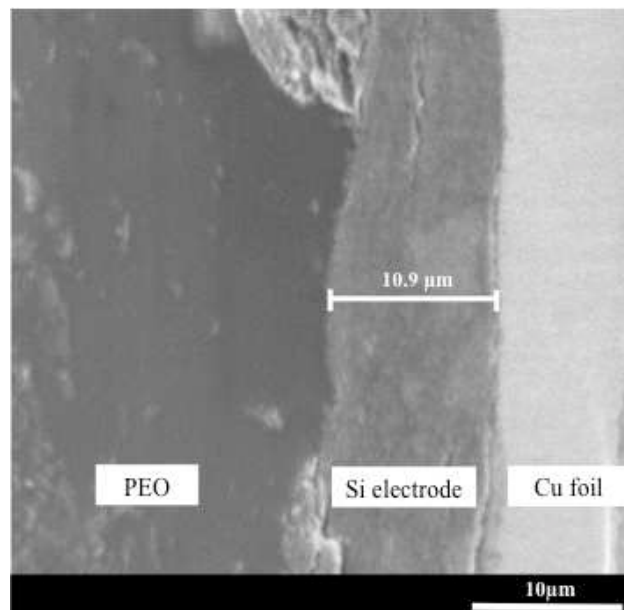
The cross sectional observation of the cell was conducted during a galvanostatic charge-discharge process.

Results and Discussion

Figure 1 shows a cross sectional observation of the electrode / electrolyte interphase, before / during charging process. The thickness of the electrode was expanded approximately 30 % after the charging process. A large crack was formed in the middle of the electrode, because the volume expansion ratio of the electrode surface should be different from the composite electrode beside current

collector. As a consequence, the internal-stress should have been generated in the electrode. Detailed observation results will be introduced at the meeting.

(a)



(b)

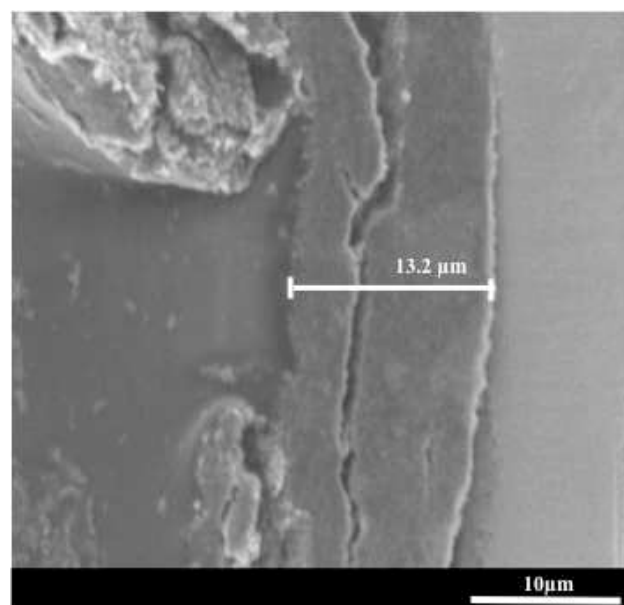


Fig.1 *in situ* SEM images for the cross section of the all-solid polymer cell before the charging process (a) and during the galvanostatic charging process (b)

Reference

- [1] M. Kawakubo, Y. Takeda, O. Yamamoto, N. Imanishi, *Journal of Power Sources*, 225 (2013) 187-191.
- [2] Q. Si, K. Hanai, T. Ichikawa, A. Hirano, N. Imanishi, O. Yamamoto, Y. Takeda, *Journal of Power Sources*, 196 (2011) 6982-6986.