Study of the Electrodeposition Process of Lithium Metal on Silicon Negative Electrodes

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Introduction

In recent years, R&D activities of lithium ion batteries for the automotive application are significantly increasing due to the commercialization of Plug-in Hybrid Vehicle and Electric Vehicle. One major problems of the lithium ion battery for automotive application is lithium deposition at the surface of graphite negative electrodes during quick charging. Since the electrodeposited lithium could initiate the short circuit resulting in the thermal runaway of the lithium-ion cell, the charging rate capability of the negative electrodes is crucial. Further more, the electrodeposition of the lithium causes the capacity decay of the cell, because the reversible lithium source is consumed by the electrodeposition [1]. Even though silicon based anode active materials is expected as a high-energy advanced negative electrode for the lithium ion battery, the lithium deposition process on silicon negative electrode has never been investigated well yet. Here we conducted the observation of the electrodeposition process of lithium metal at the surface of the silicon negative electrodes.

Experimental

An electrode-slurry was prepared by mixing 60 wt % of nano-silicone powder (particle size 100nm) as an active material, 20 wt % of polyimide (PI) binder and 20 wt % of acetylene black or carbon nanofiber as an electro-conductive material. The slurry was cast on a copper foil. After drying the electrode, it was annealed in an oven at 350℃ for 3h in vacuum. In order to study the lithium deposition process of the silicon negative electrode, coin cells were fabricated using the prepared electrode and lithium foil. The electrolyte solution used in this study is 1 M lithium hexafluoro phosphate ($LiPF_6$) dissolved in the fluoroethylene carbonate (FEC) and dimethyl carbonate (DMC) mixed solvent. The cells were galvanostatically charged and discharged at C/20 of C rate, and then the lithium deposition properties were investigated. After the lithium deposition test, coin cell was disassembled and the morphology of the electrode was observed using SEM.

Results and Discussion

Fig. 1 shows the cycling performances of the Si negative electrodes using PI and PVdF. The electrode using PVdF showed very poor capacity retention and cycling performance while the electrode using PI showed significant improvement in cycling performance. Initial capacity can reach 3000 $mAhg^{-1}$ at C/20 of charge-discharge rate. After 100 of cycles, the capacity retention rate was approximately 85%. Therefore, the electrode was sufficiently stable to be used for the lithium deposition study.

The SEM images of the silicon negative electrode and graphite after the lithium deposition test are shown in Fig. 2. The electrodes were fully charged at C/2 or 2C. The deposition temperature was 0℃. At C/2, only a slight morphology change was observed in the case of the silicon negative electrode, while significant amount of lithium dendrites were observed at the surface of graphite negative electrode. In addition, the current density for the silicon negative electrode was nearly twice as high as that of the graphite electrode. It indicates that the silicon could be a suitable negative electrode for the high power applications such as automotive batteries.

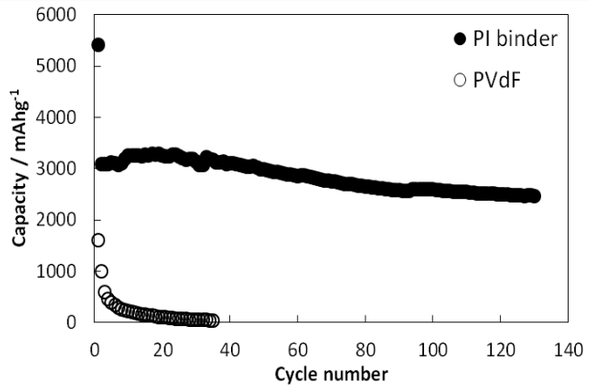

Fig.1 Cycle performance of the silicon negative electrode with PI binder or PVdF charged and discharged at C/20 rate with cut-off 0-1.5V vs. Li

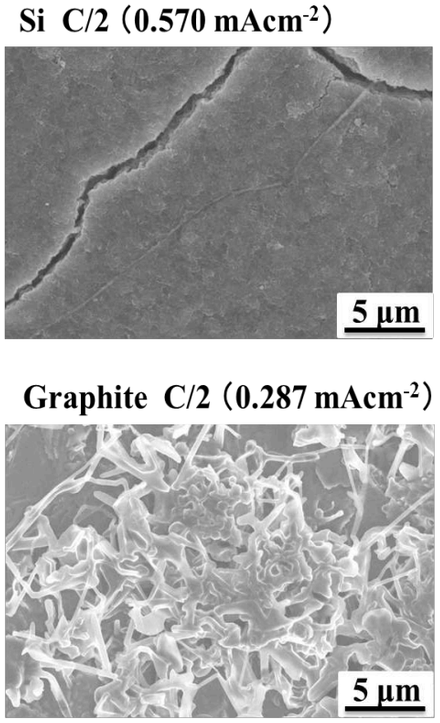

Fig.2 SEM images of silicon negative electrodes and graphite negative electrodes fully charged at C/2 at 0 ℃

Reference

[1] H. Honbo, K. Takei, Y. Ishii and T. Nishida, *J. Power Sources*, **189** (2009) 337-343