Improvement of discharge properties of thin-film lithium rechargeable battery with thicker cathode film for higher capacity

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1. Introduction

Organic (liquid) materials are generally used as the electrolytes for lithium-ion batteries. It is well known that organic materials have flammability and therefore lithium ion batteries have a problem in terms of safety. So, it is expected that practical application of the lithium secondary batteries with the solid electrolytes in order to solve this problem. All-solid-state lithium thin-film batteries (TFBs) are expected to apply to many electrical applications (wireless sensors, smart card, etc.), because of their advantage of safety and form factor based on the solid electrolyte. Lithium cobalt oxide (LCO) is used for cathode material in our experiment. We are trying to raise the discharge capacity per unit area by increasing thickness of the LCO, but there are some issues to improve. In this study, we investigated the influence of LCO film thickness on cell characteristics and also tried to improve the discharge properties.

2. Experimental

LCO cathode film was prepared by RF and DC hybrid power magnetron sputtering method on Pt film as current collector. Ar was just used as sputtering gas, and chamber pressure was kept at 3.0 Pa. After deposition, LCO was annealed at 600deg.C under atmospheric pressure by lamp heating system. LCO film thickness was ranged from 3 to 20 µm. Solid electrolyte (Lithium Phosphorus Oxynitride; LiPON) was prepared by RF magnetron reactive sputtering method with nitrogen gas. Anode (lithium; Li) films were prepared by vacuum evaporation method. Direct encapsulation stacks were formed using vapor deposition polymerization method. TFB cells were investigated by electrical and electrochemical properties at room temperature in a glove box with Ar atmosphere.

3. Results and discussion

Figure 1 shows the discharge capacity when current density was changed (LCO thickness is from 3 to 20 µm, Li thickness is 2 µm). The charge method is CCCV (Current: 0.21 mA/cm², Cut off voltage: 4.2 V, 0.021 A/cm²). The discharge method is CC (Current: x mA/cm², Cut off voltage: 3.0 V). The capacity density decreased in same current density with the LCO film thickness was decreased. It is thought that the phenomenon is due to the limitation effect of Li ions diffusion inside the LCO film, because the diffusion distance (film thickness) increased.

Figure 2 shows properties of cycle performances when lithium thickness was 2 µm. The discharge current density is 0.21 mA/cm². The capacity loss rate was increased with LCO film thickness was increased. If LCO thickness was 20 µm, the capacity was lost by about 20% after 20 charge-discharge cycles. It is thought that the segregation of lithium occurred when lithium was extracted by charge sequence, and therefore, the contact area between anode and electrolyte decreased and the capacity also decreased. Figure 3 shows properties of cycle performances when lithium thickness was 2 µm with and without direct encapsulation onto lithium. It was found that the cycle characteristics were improved by the addition of direct encapsulation onto lithium. It is considered that the segregation of lithium during charge-discharge cycles was suppressed by the contact of encapsulation stacks with lithium anode surface.

References:
1) Mamoru Baba: “Solid state film secondary battery and high-functionalization”, one of new technology symposiums by Japan Information Center of Science and Technology.
2) “Development of the all solid-state lithium ion battery (I)”, etc., research report of Central Res. Inst. of Electric Power Industry (in Japanese).

![Fig. 1. Current density vs. discharge capacity of TFB cell with 2-µm-thick Li anode and LCO thickness; (a)3 µm, (b)10 µm, (c)20 µm.](image1)

![Fig. 2. Cycle performances of TFB cells with 2-µm-thick Li anode and LCO thickness; (a)3 µm, (b)10 µm, (c)20 µm.](image2)

![Fig. 3. Cycle performances of TFB cells with 20-µm-thick LCO and 2-µm-thick Li anode, with and without encapsulation.](image3)