Preparation of All-solid-state Thin Film Rechargeable Lithium Batteries and their Electrochemical Properties

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Introduction

Rechargeable lithium batteries have been widely used in portable devices, such as cellular phones, notebook computers, video cameras, etc. Moreover, they have received much attention as a power source for hybrid and pure electric vehicles in recent years. Commercially available rechargeable lithium batteries mainly contain volatile and inflammable organic solvents, which could cause leakage of electrolyte and severe fire. These should be crucial problems for large-sized rechargeable lithium batteries requiring higher safety and reliability.

An effective way to overcome these problems is to replace organic liquid electrolyte with incombustible solid electrolyte. However, all-solid-state lithium-ion batteries have another problems, that is, lower ionic conductivities of solid electrolytes and the large charge transfer resistance at the electrode/solid electrolyte interface. In this work, we focused on the later issue and prepared all-solid-state rechargeable thin film batteries consisting of *c*-axis oriented $LiCoO_2$ thin films (referred to as *c-film* in the later description) as a positive electrode, LiPON[1] as an electrolyte, and lithium metal as an negative electrode. Because of its unique texture, electrochemically active surface area on the c-film is small. This feature is quite effective to study the charge transfer resistance at $LiCoO_2$/LiPON in detail.

Experimental

Preparation conditions of the *c-film* have been described elsewhere[1]. After the *c-film* (ca. 0.1 □m) was deposited on a platinum substrate, the *c-film* was covered with LiPON thin film (ca. 2.7 □m) by RF magnetron sputtering. Resultant samples were heat-treated at 473 K for over 15 min. in air. Lithium negative electrodes were deposited on the LiPON films by thermal evaporation and all-solid-state thin film rechargeable lithium batteries were fabricated (electrode area:0.25 cm^2). Thermal-treated LiPON films were characterized by X-ray diffraction measurement and X-ray photoelectron spectroscopy. Electrochemical measurements of thin film batteries were conducted by cyclic voltammetry and charge-discharge test. The LiPON/$LiCoO_2$ interfacial resistance was studied by AC impedance method.

Results and discussions

Figure 1 shows cyclic voltammograms of as-deposited and thermal treated (473 K for 30 min. or 60 min.) thin film batteries. Although as-deposited film battery obtained quite poor electrochemical performances, thermal treatment greatly enlarged its redox peaks [2]. Thermal-treated film batteries obtained three redox peaks assigned to the phase transition of $LiCoO_2$ were observed at around 3.90, 4.08, and 4.18 V [3]. As shown in this figure, the current peaks also increased by extending thermal treatment time.

Impedance measurements were conducted to measure the LiPON/$LiCoO_2$ interfacial resistance. In each impedance spectrum, semicircle assigned to the lithium ion transfer resistance in LiPON film was observed at high frequency region. This electrolyte resistance did not largely change by these thermal treatments. Although charge transfer resistance at LiPON/Li interface was also examined by using Li/LiPON/Li cell, this resistance was smaller than that of LiPON film. From these results, semicircle due to the charge transfer resistance at LiPON/$LiCoO_2$ was assigned. Variations of charge transfer resistances and interfacial resistivities with the thermal treatment time are summarized in Table I. The interfacial resistivity was drastically decreased with extending thermal treatment time. This tendency can explain the results of Figure 1 qualitatively.

As mentioned above, thermal treatments applied in this work did not affect the ion conductivity in LiPON film. Hence, these results clearly revealed that thermal treatment was quite effective to decrease the LiPON/$LiCoO_2$ interfacial resistance.

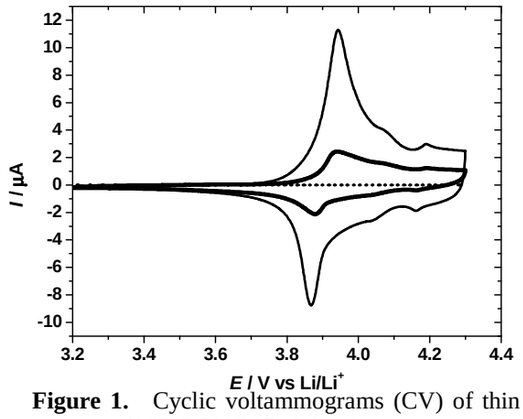

Figure 1. Cyclic voltammograms (CV) of thin film batteries (Li/LiPON/$LiCoO_2$) with thermal treatments at 473 K in air for 30 min. (bold line) and 60 min. (thin line). CV of as-deposited film battery is shown as dotted line. v = 1 mV/s.

Table I Summary of interfacial resistivities at LiPON/$LiCoO_2$ vs. thermal treatment time.

	LiPON/$LiCoO_2$		
Thermal treatment time (min.)	15	30	60
S (cm^2)	0.25		
R (□)	30000	11000	500
Interfacial resistivity (□ cm^2)	7500	2750	125

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