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Improved performance of all-solid-state lithium batteries using LiPON electrolyte prepared with Li-rich sputtering target

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ABSTRACT

Li-compensated LiPON (Li-LiPON) thin film solid electrolyte has been deposited by sputtering a sintered Li-rich $Li_{3.3}PO_4$ target instead of the normally Li_3PO_4 target, showing an improved Li ionic conductivity of 3.2×10^{-6} S/cm. All-solid-state thin film lithium batteries (TFLBs) with the structure of Si/SiO_2/Ti/Au/$LiCoO_2$/LiPON/Li have been fabricated by adopting Li-LiPON and normal LiPON (N-LiPON) electrolyte layers, respectively. The galvanostatic cycling tests show much better rate performance and higher capacity retention ratio of TFLB with Li-LiPON electrolyte. We suggested that the Li-LiPON solid electrolyte helps to reduce the space-charge layer effect induced by Li ionic defects.

1. Introduction

With the rapid development of portable electronic devices in recent years, the demand of rechargeable batteries with higher energy density is growing sharply. Among the various battery technologies, the all-solid-state thin film lithium battery (TFLB) is known as a promising candidate for micro-power applications [1]. It has broad prospects for use in smart cards, radio frequency identification, portable electronic devices, and other micro-electromechanical systems as the on-chip or lab-on-chip power source. A typical TFLB consists of a cathode layer, an electrolyte layer and an anode layer, with the total thickness around few tens of micrometers. All the three functional layers are completely in a solid state and can be fabricated in a variety of shapes, keeping away from liquid leakage during the operation. As for the TFLB, the lithium (Li) metal was chosen as anode without the worry about internal short-circuit problem caused by Li dendrites [2]. And $LiCoO_2$ has been widely used as a thin film cathode due to its high specific capacity (above 145 mAh/g) and high operating voltage ($\sim$ 3.7 V) [3,4].

Amorphous lithium phosphorus oxynitride (LiPON) thin film as an electrolyte layer was reported by the Oak Ridge National Laboratory for the first time [5], which was deposited by radio frequency (RF) magnetron sputtering from Li_3PO_4 target in a pure N_2 gas atmosphere. Furthermore, Fu et al. suggested that LiPON thin films are high-*k* materials [6]. Although LiPON shows the relatively low Li ionic conductivity of $1 - 3 \times 10^{-6}$ S/cm at 25 °C [7], it has the good chemical stability with the Li metallic anode, and the broad electrochemical potential window of 0–5.5 V (versus Li/Li^+), making it a competitive electrolyte material [8]. There were many studies on the optimization of LiPON electrolyte layer in the past years, especially on the improvement of Li ionic conductivity, including the investigation on the deposition condition [9,10] and the optimization of thickness [11]. It was found that the quality of LiPON thin film is highly sensitive on sputtering power, pressure, N_2 gas atmosphere and deposition rate, etc [12]. For instances, Choi et al. pointed out that LiPON thin film fabricated by the low power has the high ionic conductivity [13], and Haruta et al. demonstrated a very low interface resistance (8.6 Ω· cm^2) between LiPON electrolyte and $LiCO_2$ cathode [14]. These results have attracted more interest to develop the TFLB with a structure of $LiCoO_2$/LiPON/Li.

Although it has been reported that Li-compensated LiPON (Li-LiPON) thin films deposited using unsintered Li-rich targets fabricated by mixture powders of Li_3PO_4 and Li_2O would improve the Li ionic conductivity [15], the study on the device performance of TFLB using Li-LiPON electrolyte (Li-TFLB) is still absent except for a thin film battery based on Si-doped LiPON and Si-V negative electrode [16]. In this work, therefore, we firstly prepared the normal LiPON (N-LiPON) and Li-LiPON electrolytes to compare the Li ionic conductivity, and then fabricated Li-TFLB (using Li-LiPON electrolyte) and N-TFLB (using N-LiPON electrolyte) devices to investigate their cycle performance. Our results indicate that the Li-LiPON thin film not only increases the Li ionic conductivity of electrolyte layer, but also improves the rate performance and the capacity retention ratio. The first cycle discharge

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capacity at 0.1 C of Li-TFLB is 64.5 μAh·cm^{-2} · μm^{-1}.

2. Experimental

As for the electrolyte layers, LiPON thin films were deposited by RF magnetron sputtering with the sputtering power density of 2.7 W/cm^2 in the pure N_2 gas atmosphere. N-LiPON and Li-LiPON electrolyte layers were obtained by using Li_3PO_4 and $Li_{3.3}PO_4$ targets, respectively. The Li_3PO_4 target was prepared by pressing of Li_3PO_4 powder (purity 99.99%) into a 75 mm diameter pellet and sintering at 750 °C for 4 h. While $Li_{3.3}PO_4$ target was prepared by mixing of Li_3PO_4 powder (purity 99.99%) and Li_2O powder (purity 99.99%) at the molar ratio of 6.67 : 1 for Li_3PO_4 : Li_2O, followed by the similar pressing and sintering process as for the Li_3PO_4 target. In order to optimize the Li ionic conductivity of the electrolyte layer, a series of LiPON thin films have been deposited under the working pressure varying from 0.5 to 0.08 Pa.

To fabricate TFLB devices, the Au film of 0.1 μm thickness was deposited on a Si/SiO_2/Ti substrate by the thermal evaporation as a current collector layer. After that, $LiCoO_2$, LiPON and Li layers were deposited in sequence on the Au film. Specifically, the $LiCoO_2$ thin film with the thickness around 0.45 μm was deposited by RF magnetron sputtering in the mixture of Ar and O_2 gas atmosphere with the sputtering power density of 3.4 W/cm^2 and the working pressure of 0.3 Pa, using a $LiCoO_2$ target (purity 99.99%). The flow rate ratio between Ar and O_2 was set as 3 : 1. The as-deposited $LiCoO_2$ cathode layer was annealed at a temperature of 700 °C for 1 h to obtain a better crystalline phase. The optimized N-LiPON and Li-LiPON electrolyte layers were then deposited upon the same batch of $LiCoO_2$ cathode layers, respectively. Finally, the Li thin films were deposited by the thermal evaporation as the anode layers.

The microscopic structure and thickness of the films were studied by the field emission scanning electron microscopy (FE-SEM: Hitachi, S-4800). The Li ionic conductivity of each LiPON electrolyte was obtained from the AC-impedance measurement of Cu/LiPON/Cu sandwich structure with a surface area of 49 mm^2 which was fabricated on the glass substrate. And the Cu electrode with a thickness around 200 nm was deposited by RF magnetron sputtering. The electrochemical impedance spectra (EIS) was obtained by applying an AC voltage with an amplitude of 10 mV in the frequency range from 1 Hz to 5 MHz at room temperature using electrochemical workstation (Zahner Zennium, Germany). To analyze the cyclic performance of TFLB, the discharge-charge tests were performed under selected constant current densities in the voltage window of 3.2–4.2 V by using potentiostat-galvanostat apparatus.

3. Results and discussion

3.1. Growth of thin films and fabrication of TFLB

The cross section view of functional layers of the TFLB and the plan view of $LiCoO_2$ and Li-LiPON are presented in Figs. 1 and 2, respectively. The $LiCoO_2$ thin film was deposited on Au substrate by RF sputtering. As shown in Figs. 1 (a) and 2(a), after being annealed at 700 °C in the air for 1 h, the $LiCoO_2$ cathode layer has the smooth surface and the good quality of crystalline. In order to investigate the Li ionic conductivity of LiPON electrolyte layers, samples with Cu/LiPON/Cu sandwich structure were fabricated on glass substrates. The typical thickness of a deposited LiPON thin film is around 2 μm as shown in Fig. 1 (b). Seen from the surface SEM image of the Li-compensated electrolyte shown in Fig. 2 (b), the surface of Li-LiPON thin film is smooth. Fig. 2 (c) and (d) exhibits the 2D and 3D atomic force microscope (AFM) images of Li-LiPON thin film, respectively. The root mean square roughness is about 0.17 nm and the biggest height of surface undulation is only 1.6 nm on the Li-LiPON thin film. For obtained LiPON thin films, we have investigated the element ratio by performing the inductively coupled plasma (ICP) measurement to analyze the Li content in LiPON electrolyte layer. We found that the molar ratio of Li/P is 2.49 for N-LiPON while this value is 2.98 for Li-LiPON. The result indicates that the Li content does increase in Li-LiPON fabricated by Li-rich target and it is close to the stoichiometry of 3. After the optimization of each functional layer, the TFLB with the structure of Si/SiO_2/Ti/Au/$LiCoO_2$/LiPON/Li was fabricated to study the effect of Li-compensated electrolyte on the device performance. The cross section SEM view of Li-TFLB in Fig. 1 (c) shows the thicknesses of $LiCoO_2$ cathode layer and Li-LiPON electrolyte layer are about 0.45 μm and 1.49 μm, respectively.

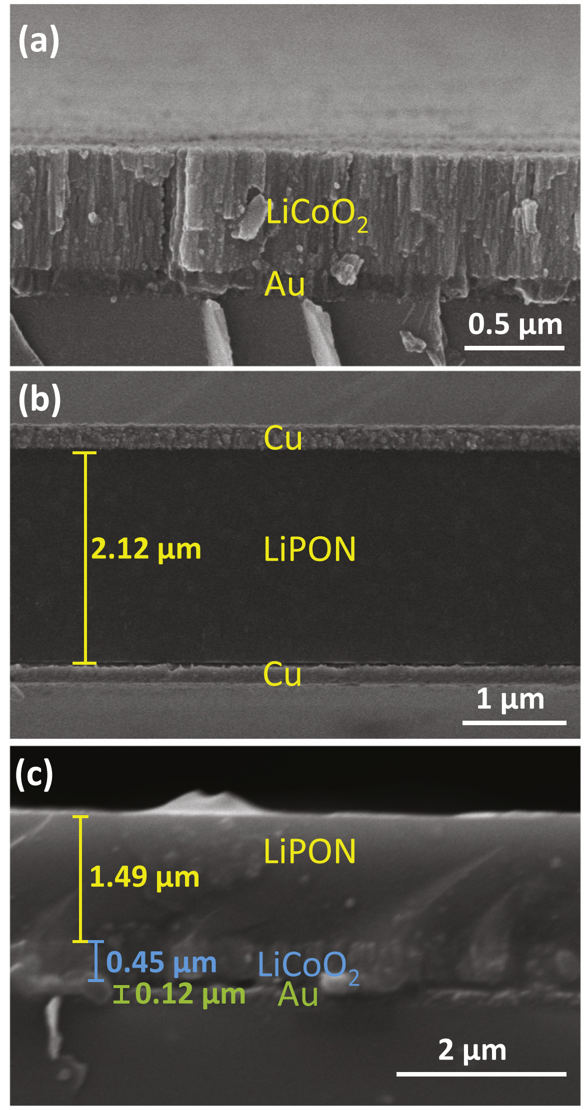

Fig. 1. The cross-sectional SEM images of $LiCoO_2$ cathode layer annealed at the temperature of 700 °C for 1 h (a), Cu/LiPON/Cu sandwich structure fabricated on the glass substrate (b) and TFLB with the structure of Si/SiO_2/Ti/Au/$LiCoO_2$/Li-LiPON (c).

3.2. Properties of LiPON electrolyte layers

Fig. 3(a) shows the complex impedance diagram for N-LiPON electrolyte layers which were deposited under various working pressures. The EIS for each LiPON electrolyte layer consists of a semicircle in the high-frequency region which is assigned to the bulk LiPON and a straight line in the low-frequency region corresponding to the interfaces between the LiPON and adjacent Cu electrodes. Accordingly, the electrical response of each sample is described by a possible equivalent