Short communication

Investigation of interfacial resistance between LiCoO$_2$ cathode and LiPON electrolyte in the thin film battery

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Abstract

All solid-state thin film battery was prepared with conventional sputtering technologies. Low conductivity of lithium phosphorus oxynitride (LiPON) electrolyte and higher resistance at the interface of LiCoO$_2$/LiPON was crucial for the development of thin film battery. Presence of thermally treated Al$_2$O$_3$ thin film at the interface of LiCoO$_2$/LiPON decreased the interfacial resistance and increased the discharge capacity with the better cycling behaviors. Surface analysis and electrochemical impedance measurement indicate the formation of solid solution LiCo$_{1-y}$Al$_y$O$_2$ at the interface of LiCoO$_2$/LiPON.
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1. Introduction

Microenergy power sources need to be developed to drive small microelectronic devices such as smart card and micro-electromechanical systems [1]. All solid-state thin film battery that can be fabricated by thin film deposition technology has been known as the best candidate for small power supplier. Thin film battery can be fabricated with a few micrometers thick to be fitted for any required size and shapes. LiCoO$_2$ has been studied extensively and considered as a cathode material for its high capacity and high energy density and, lithium phosphorous oxynitride (LiPON) has been known as a stable and relatively high ionic conducting solid electrolyte [2,3]. However, lower ionic conductivities of solid electrolyte than liquid electrolyte and large charge transfer resistances at the electrode/electrolyte interface limited the practical applications of thin film battery [4]. Bates et al. and Ogumi et al. elucidated that the thermal treatment of LiCoO$_2$/LiPON decreased the cell resistance substantially [5,6].

Removal of Li$^+$ from Li$_x$CoO$_2$ ($x < 0.25$) induces the oxidation of Co^{3+} to Co^{4+}, which results in the significant decrease of c-axis dimension when the charging voltage is above 4.5 V ver-

sus Li. This phenomenon may cause the rapid capacity fading of battery [7]. Coating of LiCoO$_2$ with metal oxides, such as Al$_2$O$_3$, ZrO$_2$, and AlPO$_4$, has been suggested to improve the structural stability during cycling by the formation of solid solution at the LiCoO$_2$/metal oxides interface [8–11]. Since solid-state system has difficulties in managing good solid–solid contacts with low interfacial resistances which permits a high degree of reversibility, control of electrode/solid electrolyte interface is very important for the enhancement of power density of all solid-state rechargeable lithium batteries.

Al$_2$O$_3$ coating onto LiCoO$_2$ exhibited excellent capacity retention in a rechargeable lithium ion battery using liquid electrolyte [11]. In this work, nanometer-thick Al$_2$O$_3$ is deposited onto LiCoO$_2$ to improve structure stability and control the LiCoO$_2$/LiPON interfacial resistance. LiCoO$_2$/Al$_2$O$_3$ was thermally treated to reduce the interfacial resistance and the effect of cyclic voltammetry on the thin film battery performance was investigated using electrochemical impedance spectroscopy (EIS) measurement.

2. Experimental

Pt (2500 Å)/Ti (500 Å) current collector layers were deposited on a Si(1 0 0) wafers by direct current (dc) sputtering method. 0.5 μm thick LiCoO$_2$ films were deposited by rf magnetron sputtering in an Ar gas atmosphere at the working

pressure of 10 mTorr during deposition. The rf power was 300 W. Al_2O_3 (100 Å) film was prepared at room temperature by rf magnetron reactive sputtering with Al_2O_3 target. The flow rates of O_2 and Ar were 153 sccm and 17 sccm, respectively, and the rf power was 150 W. The Al_2O_3 target surface was pre-sputtered by Ar^+ plasma to eliminate an oxide layer on the target surface for 5 min. $LiCoO_2$ or $LiCoO_2/Al_2O_3$ were thermally treated at 673 K for 5 h and cooled down to room temperature. LiPON (1.2 μm) solid electrolytes were deposited by rf magnetron reactive sputtering of a Li_3PO_4 target in a N_2 gas condition. On sputtering in 4N purity pure nitrogen, the surface of the Li_3PO_4 target becomes nitrided. The lithium anode is deposited by thermal evaporation to 2 μm thickness.

The ac impedance of the films was measured by a frequency response analyzer (Zahner IM6) in the frequency range from 100 mHz to 10^6 Hz. The crystal structure and compositional depth profile of the film was observed with an X-ray diffractometer (XRD, Philips DY616) and Auger electron spectroscopy (AES, Perkin-Elmer PHI-670). The charge–discharge characteristics were carried out with a cycler (WBCS3000, Wonatech) operating at constant current. The current density and cutoff voltage range were 25 μA/cm² and 3–4.2 V, respectively.

3. Results and discussion

3.1. Conductivity of LiPON electrolyte

The impedance spectrum of Pt/LiPON/Pt in Fig. 1 is in agreement with the typical blocking electrode type behavior in the entire frequency range [4]. When potential was scanned from open circuit voltage to 5 V at 1 mV s⁻¹, the impedance measurement does not indicate the formation of a resistive layer at the interface but the conductivity of LiPON increased with the increase of potential scans. Fig. 1 indicates that the conductivity of as-deposited LiPON is 4.62×10^{-7} S cm⁻¹ and increases to 4.92×10^{-7} S cm⁻¹ with the first scan. Two successive potential scan increases the conductivity up to 6.25×10^{-7} S cm⁻¹.

Fig. 1(d) shows that the bias sputtering induces the substantial increase of conductivity from 4.62×10^{-7} S cm⁻¹ to 1.16×10^{-6} S cm⁻¹. Bias voltage of −60 V to −100 V on substrate makes the uniform distribution of LiPON by ion bombardment and the simultaneous increase of nitrogen content during reactive sputtering. It is not clear yet that potential scan induces the similar effect like the bias sputtering. Bias sputtering has a limitation in practical use because it removes the pre-deposited $LiCoO_2$ cathode during LiPON deposition in the process of full cell fabrication.

3.2. Effect of Al_2O_3 thin film existing at the $LiCoO_2$/LiPON

Excellent capacity retention ability of Al_2O_3 in a rechargeable Li-ion battery using liquid electrolyte is applied to all solid-state battery. Fig. 2 suggests that as-deposited Al_2O_3 thin film works as both resistive layer for ionic conductivity and charge transfer resistance layer because of insulating property. When it is thermally treated at 673 K for 5 h, Fig. 3 indicates that a small semi-circle at high frequency remains and others are disappeared. This impedance behavior is almost equivalent to the cell in Fig. 2(a) without Al_2O_3. It suggests the formation of solid solution $LiCo_{1-y}Al_yO_2$ at the interface during heat treatment, which improves the structural stability during cycling [8]. The transformation of Al_2O_3 thin film to $LiCo_{1-y}Al_yO_2$ implies that Al_2O_3 does not work as a resistive layer anymore. Compositional analysis of thermally treated $LiCoO_2/Al_2O_3$ along the depth was executed with AES, as shown in Fig. 4. Aluminum was found at the depth of ∼170 Å (sputtering rate = 35 Å min⁻¹), which suggests the incorporation of Al inside $LiCoO_2$ to form solid solution.

Fig. 5 shows the charge–discharge curve of a thin film $LiCoO_2$ (5000 Å)/Al_2O_3/LiPON (1.2 μm)/Li (2 μm) cell at the 25 μA cm⁻². Thermally treated Al_2O_3-coated $LiCoO_2$ thin film battery shows better capacity than as-deposited Al_2O_3. Cyclic voltammograms of the cell without Al_2O_3 interlayer (cell A) was compared with the cell with thermally treated Al_2O_3 interlayer
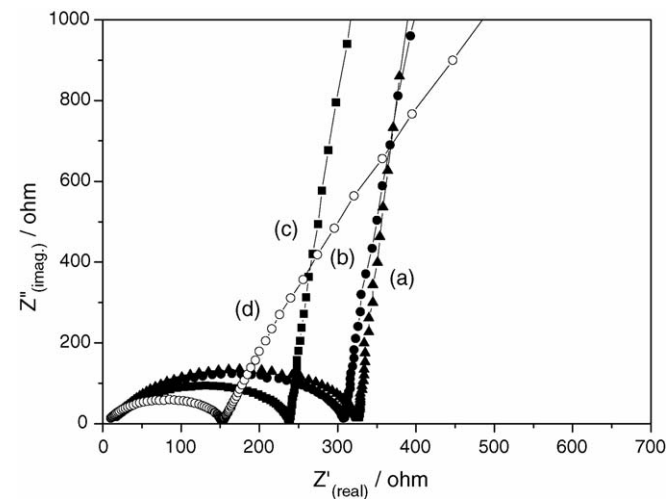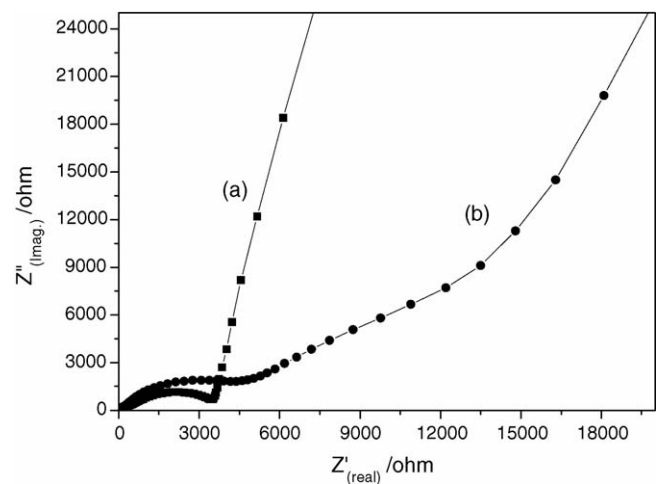

Fig. 1. Impedance spectra of Pt/LiPON/Pt. Potential was scanned from OCV to 5 V at 1 mV s⁻¹. (a) As-deposited (▲), (b) after single potential scan (●), (c) after two successive potential scans (■), and (d) after bias sputtering (○).

Fig. 2. The effect of Al_2O_3 interlayer intervened between $LiCoO_2$ and LiPON on the impedance spectra of thin film battery (basis: $LiCoO_2$/LiPON/Li). (a) Basis and (b) Al_2O_3 interlayer.
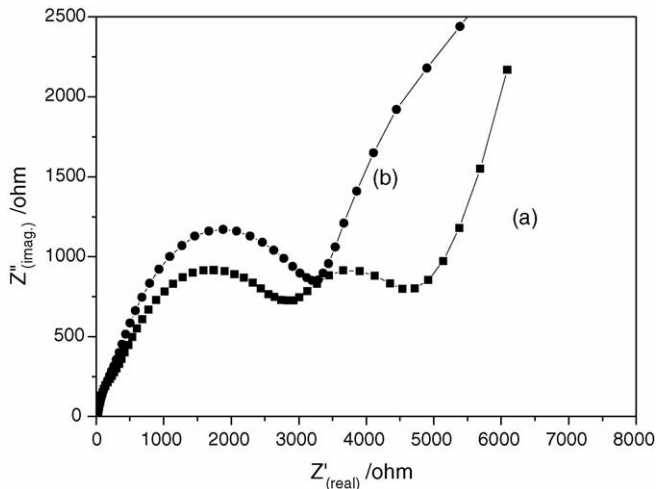
Fig. 3. Impedance spectra of the Pt/LiCoO$_2$/Al$_2$O$_3$/LiPON/Li: (a) Al$_2$O$_3$ as-deposited and (b) Al$_2$O$_3$ with thermal treatment at 673 K for 5 h.
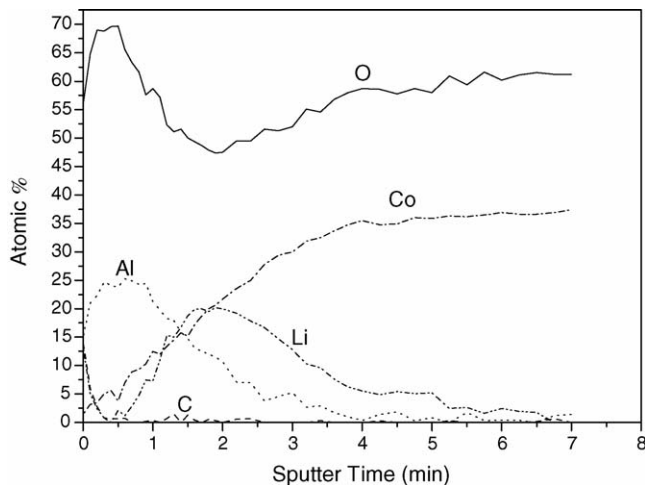

Fig. 4. AES depth profile of LiCoO$_2$/Al$_2$O$_3$ (Al$_2$O$_3$ is thermally treated at 673 K for 5 h).
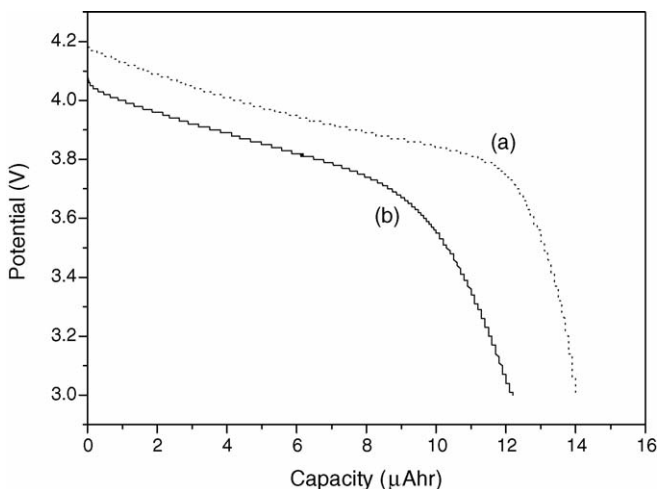

Fig. 5. Potential–capacity curves of the LiCoO$_2$ in thin film battery: (a) Al$_2$O$_3$ with thermal treatment and (b) Al$_2$O$_3$ as-deposited.
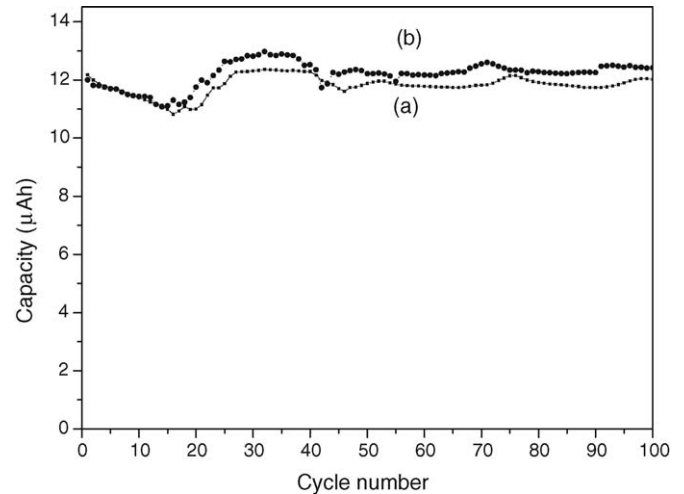

Fig. 6. Cyclability data for thin film battery: cutoff voltage of 3.0–4.2 V. (a) Without Al$_2$O$_3$ and (b) with thermally treated Al$_2$O$_3$.

(cell B). The amount of charging during CV was 0.146 C for Al$_2$O$_3$-coated cell and 0.129 C for the cell without Al$_2$O$_3$. Fig. 6 shows the cycling behaviors for the cells A and B. The cell B has higher capacity and more stable than cell A up to 100 cycles. It can be assumed that the good cycling performance is due to the maintenance of LiCoO$_2$ structure and the small variation of surface morphology that results in the capacity increase. The presence of LiCo$_{1-y}$Al$_y$O$_2$ may be responsible for the capacity increase, too.

4. Conclusions

A few micrometers thick solid-state battery was fabricated with rf magnetron sputtering for LiCoO$_2$ and Al$_2$O$_3$, reactive sputtering for LiPON, and thermal evaporation for Li metal. Lower ionic conductivities of LiPON can be increased with the bias sputtering. However, bias sputtering has a limitation in practical use because it removes the pre-deposited LiCoO$_2$ cathode during LiPON deposition. Al$_2$O$_3$ coating onto LiCoO$_2$ in a rechargeable Li-ion battery using liquid electrolyte has excellent capacity retention ability. This property of Al$_2$O$_3$ is applied to all solid-state batteries to solve the high resistance at the interface of LiCoO$_2$/LiPON. Thermally treated Al$_2$O$_3$ thin film at the interface decreases the interfacial resistance and increases the discharge capacity with the better cycling behaviors by the formation of solid solution, LiCo$_{1-y}$Al$_y$O$_2$.

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