Reduction of charge transfer resistance at the lithium phosphorus oxynitride/lithium cobalt oxide interface by thermal treatment

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Abstract

An all-solid-state thin-film battery consisting of a *c*-axis-oriented $LiCoO_2$ thin-film and a lithium phosphorus oxynitride (LiPON) glass electrolyte was fabricated. Thermal treatment at 473 K after fabrication of the $LiPON/LiCoO_2$ interface decreased the charge transfer resistance at the interface, and the resistance was further reduced by prolonging the thermal treatment time. The charge transfer resistance per unit electrode area (interfacial resistivity) of a film battery thermal-treated for 60 min decreased down to 125 $\Omega\,cm^2$, which is ca. five times larger than that in the case of an organic electrolyte (1 mol dm^{-3} $LiClO_4$ dissolved in propylene carbonate)/$LiCoO_2$ interface (25 $\Omega\,cm^2$). Due to the reduction of the charge transfer resistance at the $LiPON/LiCoO_2$ interface, the reaction current of the film battery was greatly increased by the thermal treatment. Also, thermally treated film batteries showed stable electrochemical lithium insertion/extraction properties compared with the batteries using conventional organic electrolytes. Both the voltammograms and the impedance spectra of the film battery maintained their initial shape for over 100 cycles, and the capacity retention ratio per cycle was calculated to be 99.9%.
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1. Introduction

Recent worldwide interest in pure electric and hybrid vehicles has accelerated the R&D of larger-sized rechargeable lithium batteries. High safety and reliability are pre-requisites for these batteries. Smaller-sized rechargeable lithium batteries are widely used in portable devices such as cellular phones and notebook computers. However, because these conventional batteries usually contain volatile and inflammable organic solvents, they can potentially leak electrolytes, resulting in severe fires. Hence, all-solid-state rechargeable lithium batteries, consisting of incombustible solid electrolytes, have received much attention in recent years. Unfortunately, all-solid-state rechargeable lithium batteries have some limitations for practical use, due to the lower ionic conductivities of solid electrolytes and large charge transfer resistances at the

electrode/solid electrolyte interface. Because of the progressive development of solid electrolytes, highly ionic conductive solid electrolyte materials have been prepared and some of them exhibit conductivities of the order of 10^{-3} $S\,cm^{-1}$ at room temperature [1–5]. As compared with these studies, there are few studies on the reduction of charge transfer resistances at the electrode/solid electrolyte interface, although this also plays an important role for the enhancement of power density of all-solid-state rechargeable lithium batteries.

Thin-film electrodes provide many advantages, particularly when studying charge transfer reactions, because such electrodes are thin and flat and obtain a uniform potential distribution [6,7]. Recently, Bates et al. prepared the thin-film batteries ($Li/LiPON/LiCoO_2$) and mentioned that thermal treatment after formation of the $LiPON/LiCoO_2$ interface drastically decreased the cell resistance [8]. Our recent work also revealed that thermal treatment is quite effective in decreasing the charge transfer resistance at the $LiPON/LiCoO_2$ interface [9,10]. However, the total

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resistance itself was not sufficiently reduced compared with of the batteries using conventional organic electrolytes.

In this work, we fabricate all-solid-state thin-film rechargeable lithium batteries (Li/LiPON/LiCoO$_2$) composed of *c*-axis-oriented LiCoO$_2$ thin films, LiPON films and lithium metal films. We reveal that the charge transfer resistance at the LiPON/LiCoO$_2$ interface is drastically decreased by prolonging the thermal treatment time. We also compared the charge transfer resistance at the LiPON/LiCoO$_2$ interface with that at an organic electrolyte (1 mol dm^{-3} LiClO$_4$ dissolved in propylene carbonate)/LiCoO$_2$ interface and discussed the stability of the electrochemical lithium insertion/extraction properties of the resultant film batteries.

2. Experimental

Thin films of *c*-axis-oriented LiCoO$_2$ (ca. 0.1 µm in thickness) were prepared on platinum substrates by pulsed laser deposition [6]. Hereafter, the *c*-axis-oriented LiCoO$_2$ thin-film is referred to as *c-film*. Lithium phosphorus oxynitride (LiPON) films were deposited on the *c-films* by RF magnetron sputtering for 30–48 h. Precise preparation conditions for these films were described elsewhere [9,10]. The resultant LiPON-coated *c-films* were placed on a hotplate preheated at 473 K for 15–60 min, and were then removed from the hotplate and cooled down to room temperature. All of these thermal treatments were conducted in air. Lithium negative electrodes were deposited on the thermally treated films in an argon-filled glove box. Thus, the all-solid-state thin-film rechargeable lithium batteries were fabricated.

The effects of thermal treatment on the ionic conductivities in LiPON films were also studied by using Pt/LiPON/Pt sandwiched cells. The sandwiched cells were fabricated by depositing LiPON films on platinum substrates, followed by depositing platinum thin films on the LiPON films by RF magnetron sputtering. Ionic conductivities of LiPON films were measured by AC impedance spectroscopy. The thermally treated LiPON films were characterized by X-ray photoelectron spectroscopy (ULVAC-PHI Model 5500, Mg source).

The electrochemical performance of the film batteries was determined by cyclic voltammetry and AC impedance spectroscopy. All electrochemical measurements were carried out in an argon-filled glove box at room temperature.

3. Results and discussion

3.1. Effects of thermal treatment on ionic conductivities of LiPON films

The impedance spectrum of an as-deposited Pt/LiPON/Pt sandwiched cell is shown by closed circles in Fig. 1. The impedance spectrum exhibited typical blocking electrode type behavior, showing one semi-circular arc (A) in the high-frequency region, followed by a straight line nearly vertical to
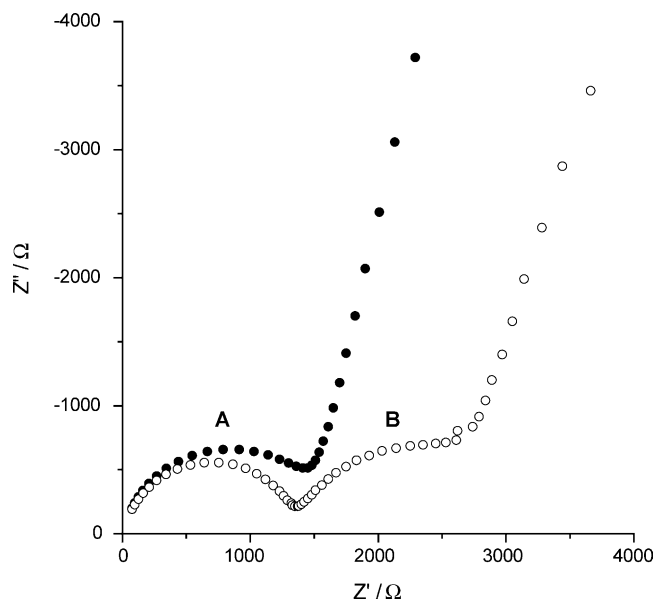

Fig. 1. AC impedance spectra of Pt/LiPON/Pt cell in an as-deposited state (closed circles) and with the thermal treatment at 473 K for 30 min in air (open circles). Platinum current collector was deposited on the thermally treated LiPON film fabricated on a platinum sheet.

the real axis. When the sandwiched cell was thermally treated for over 60 min, there were no obvious changes in the shape of the spectrum except for a slight decrease in the semi-circular arc. However, when the platinum thin films were deposited on the LiPON film after thermal treatment for over 30 min, another semi-circular arc (B) appeared in the low-frequency region, as shown by open circles in Fig. 1. This result indicates that a resistive layer is formed on the LiPON surface by the thermal treatment.

Fig. 2 shows the wide-scan XPS spectra of the LiPON films. Peak intensities in each spectrum were normalized using the strongest peak in the spectrum. On the surface of as-deposited LiPON film (Fig. 2(a)), peaks assigned to O 1s, N 1s, P 2s, P 2p and Li 1s were observed at around 530, 400, 190, 130 and 56 eV, respectively. These are elements included in the LiPON film. A peak assigned to C 1s is probably due to some adsorbed compounds including C on the LiPON film. When the film was thermally treated for over 30 min, the intensity of the N 1s, P 2s and P 2p peaks decreased on the film surface (Fig. 2(b)). After Xe ion etching for 4 min, these peaks appeared again and the strong C 1s peak also disappeared, as shown in Fig. 2(c). These results suggest that a reaction layer mainly composed of Li, O and C (Li$_2$CO$_3$, etc.) is formed on the film surface by the thermal treatment. This reaction layer will become a resistive layer for ionic conductivity, resulting in the formation of semi-circular arc (B) as given in Fig. 1.

3.2. Effects of thermal treatment time on charge transfer resistance at the LiPON/LiCoO$_2$ interface

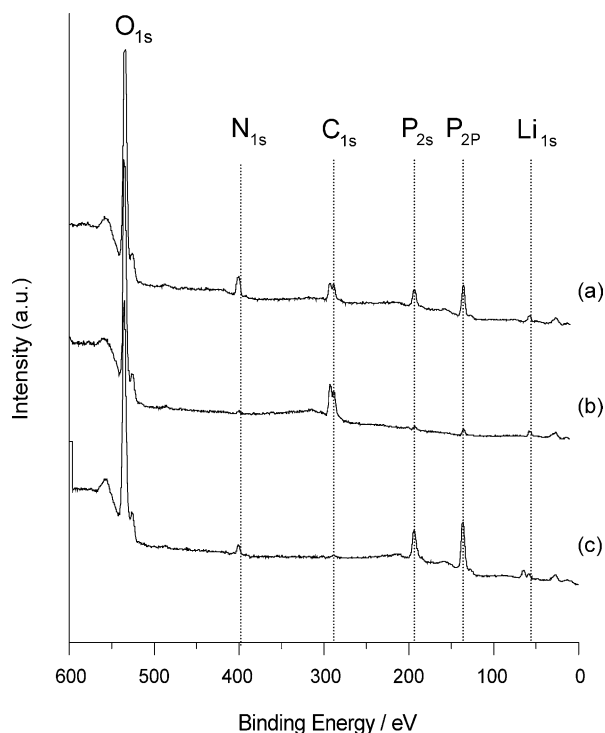Fig. 3 shows the cyclic voltammograms for film batteries with different thermal treatment times. All of these

Fig. 2. Wide-scan XPS spectra on the surface of LiPON films (a) before and (b) after thermal treatment at 473 K for 30 min. (c) Wide-scan XPS spectra of thermally treated LiPON film after Xe ion etching for 4 min.

voltammograms were collected between 3.2 and 4.3 V at $1\,mV\,s^{-1}$. Although the as-deposited film battery exhibited no visible reaction peak, the first-order phase transition peak of $LiCoO_2$ observed at 3.9 V was greatly increased by prolonging the treatment time. Peaks assigned to the phase transition between the hexagonal and monoclinic phases were also clearly observed at 4.08 and 4.18 V in the film battery with a thermal treatment of 60 min.
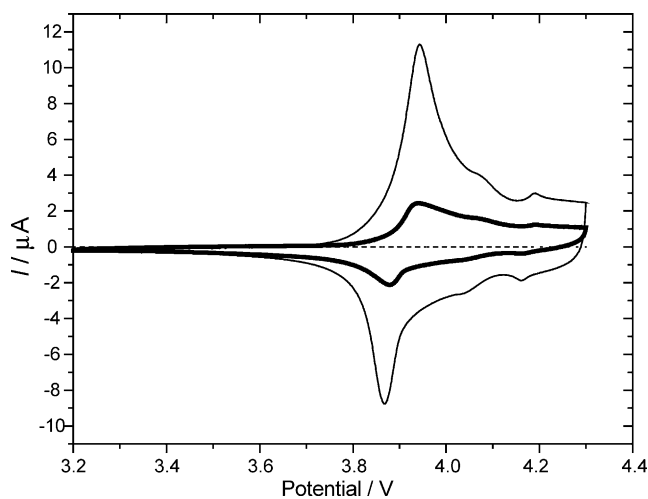

Fig. 3. Cyclic voltammograms of the film batteries. Dotted line: in as-deposited state, bold line: with thermal treatment at 473 K for 30 min and thin line: with thermal treatment at 473 K for 60 min.
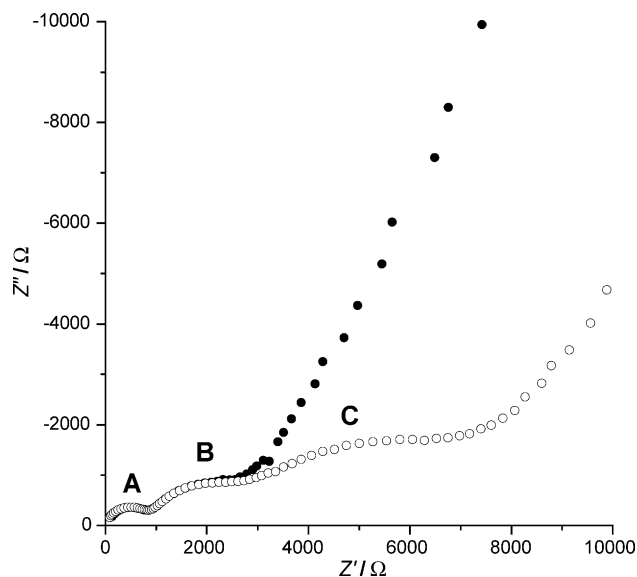

Fig. 4. Cole–Cole plot of the film batteries with thermal treatment at 473 K for 30 min; closed circles: at 3.5 V and open circles: at 4.0 V.

AC impedance measurements were carried out at 3.5 and 4.0 V in these film batteries to evaluate the charge transfer resistances. Fig. 4 shows the impedance spectra of the film battery with a thermal treatment of 30 min. Two semi-circular arcs marked by A and B were observed in the high-frequency region at 3.5 V. At this potential, electrochemical lithium insertion/extraction reactions of $LiCoO_2$ do not occur. Hence, this behavior should be related to the ionic conduction in the LiPON film. Further, the impedance spectrum at 3.5 V is very similar to the spectrum for the thermally treated sandwiched cell in Fig. 1. When the electrode potential was increased up to 4.0 V, a new semi-circular arc (C) was observed in the low-frequency region. Only this semi-circle depends on the electrode potential, indicating that the semi-circular arc (C) can be assigned to the charge transfer resistance at the LiPON/$LiCoO_2$ interface. The charge transfer resistance at the Li/LiPON interface was too small to be clearly observed as a semi-circle in this spectrum [10].

Table 1 summarizes the charge transfer resistances at LiPON/$LiCoO_2$ interfaces with thermal treatments of 15, 30 and 60 min. These resistances were evaluated from the semi-circular arc (C) in the impedance spectra. We also measured the charge transfer resistance of the *c-film* at 4.0 V in 1 mol dm^{-3} $LiClO_4$ dissolved in propylene carbonate (PC) solution. Interfacial resistivity, that is, the charge transfer

Table 1
Summary of charge transfer resistances at the electrolyte/*c*-axis oriented $LiCoO_2$ thin-film interface

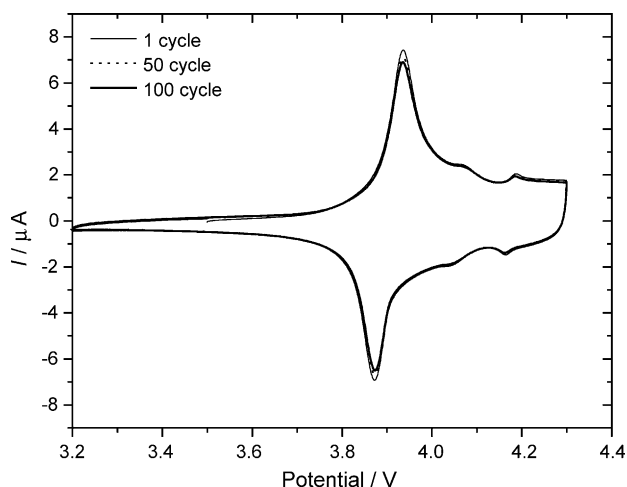| Interface	LiPON/$LiCoO_2$			PC/$LiCoO_2$
Thermal treatment time (min)	15	30	60	–
Charge transfer resistance (Ω)	31700	5500	500	125
Geometric electrode area (cm^2)	0.25	0.25	0.25	0.20
Interfacial resistivity (Ω cm^2)	7925	1375	125	25

Fig. 5. Cycle number dependency of cyclic voltammograms of the film battery with thermal treatment at 473 K for 60 min.

resistance at an electrolyte/$LiCoO_2$ interface per unit electrode area, was calculated by multiplication of the charge transfer resistance by the geometric electrode area. The interfacial resistivity at the $LiPON/LiCoO_2$ interface was drastically decreased with prolonged heat-treatment time. In this work, the resistivity decreased down to $125\,\Omega\,cm^2$, which is ca. five times larger than that of the $PC/LiCoO_2$ interface.

3.3. Electrochemical performances of thermally treated film batteries

Fig. 5 shows the cyclic voltammograms of the film battery with a thermal treatment of 60 min. The voltammogram maintained its initial flag shape for over 100 cycles. In our previous experiments [11], when the *c-film* was cycled between 3.5 and 4.2 V in conventional organic electrolytes such as $1\,mol\,dm^{-3}$ $LiClO_4$ dissolved in PC solution, the first-order phase transition peak gradually shifted in the potential sweep direction and the peak intensity also decreased. Moreover, an irreversible increase in the charge transfer resistance was observed. In contrast, the thermal-treated film battery maintained quite stable electrochemical performance, indicating that the thermally treated $LiPON/LiCoO_2$ interface can provide stable electrochemical performances compared with conventional systems using organic liquid electrolytes. Since the impedance spectrum after 100 cycles remained its initial shape, the stable reaction of the film battery is principally due to the stability of the $LiPON/LiCoO_2$ interface. The thin-film battery showed good cycle ability, and the capacity-retention ratio per cycle of the film battery was evaluated from the voltammogram to be 99.9%.

4. Conclusions

All-solid-state thin-film rechargeable lithium batteries ($Li/LiPON/LiCoO_2$) were fabricated and the effects of thermal treatment on charge transfer resistance at the $LiPON/LiCoO_2$ interface were examined. Although thermal treatment at 473 K for 60 min increased the total resistance due to the increase of the resistivity of LiPON film electrolyte, it greatly reduced the charge transfer resistance at the $LiPON/LiCoO_2$ interface. In this work, the interfacial resistivity decreased down to $125\,\Omega\,cm^2$, which is ca. five times larger than that of conventional organic electrolyte/$LiCoO_2$ systems. This interfacial resistivity can be minimized by optimizing the thermal treatment conditions. The resultant film batteries exhibited stable electrochemical performances compared with conventional systems using organic liquid electrolytes. These results will be important guidelines to develop all-solid-state lithium batteries with high power densities.

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