

Short communication

Preparation of positive LiCoO₂ films by electron cyclotron resonance (ECR) plasma sputtering method and its application to all-solid-state thin-film lithium batteries

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Abstract

Thin films of LiCoO₂ prepared by the electron cyclotron resonance (ECR) sputtering method are investigated under various deposition conditions. Well-crystallized LiCoO₂ films were obtained without a post-annealing process in a high microwave and RF power range with a low O₂ to Ar ratio. All-solid-state thin-film lithium batteries using the LiCoO₂ films (thickness: 6.2 μm) provided a discharge capacity of about 250 μAh cm⁻² with good cyclability.

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1. Introduction

Recently electronic devices such as RF ID tags and paper displays have attracted much attention as portable communication tools. There is also a strong demand to reduce the size and weight of these devices. To satisfy these requirements, it is important that we develop thin and light microbatteries for the devices. An all-solid-state thin-film lithium battery is a promising microbattery candidate. This battery has various advantages including no liquid leakage, excellent safety, a long cycle life and a wide operating temperature range [1–6]. These features make the battery very attractive as a micro power source.

If we are to apply thin-film batteries to electronic devices we must first increase the battery capacity and reduce the production cost. These problems can be overcome by preparing a thicker positive oxide film by using a process that does not involve post-annealing in an electric furnace. Such a process makes it possible to form the batteries on flexible polymer substrates, instead of the conventionally used metal or glass substrates. Thin-film batteries formed on flexible substrates would find a wide range of uses in various devices because of their ease of handling.

In research on lithium secondary batteries, LiCoO₂ has been widely used as the positive electrode material due to its ease of preparation, high voltage, high specific capacity, and long stable cycle life. LiCoO₂ thin films are conventionally deposited by using both dry and wet processes such as the radio frequency (RF) magnetron sputtering method [3–7], pulsed laser deposition (PLD) [8–10] and the sol–gel method [11]. However, in many previous reports on these methods, a post-annealing process is employed to crystallize the as-deposited amorphous-like oxide films. In reports on LiCoO₂ preparation by the PLD method, the crystallization of LiCoO₂ films was enhanced by keeping the substrates at elevated temperatures of 600–700 °C during the deposition. We prepared LiCoO₂ films using an electron cyclotron resonance (ECR) plasma sputtering method. To our knowledge, there have been no previous reports on LiCoO₂ films prepared by this method. The oxide film can be deposited under high-energy ionic radiation with this method [12]. This means that crystalline LiCoO₂ film can be prepared at a lower temperature thus avoiding the possibility of distorting the polymer substrate.

We investigated the conditions for preparing LiCoO₂ films by the ECR plasma sputtering method. Thin-film lithium batteries were prepared by depositing LiPON electrolyte (Li ion conductor) and metallic negative Li film on positive LiCoO₂ films. We investigated the electrochemical properties of thin-film

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batteries using LiCoO₂ films prepared under appropriate sputtering conditions.

2. Experimental

A schematic illustration of the ECR plasma sputtering equipment (NTT AFTY Co., AFTEX-EC3400R) is shown in Fig. 1. ECR plasma is generated by introducing microwaves (2.45 GHz) into a magnetic field produced by applying electric currents to a coil under an Ar and O₂ gas flow. The ECR plasma, which includes argon and oxygen, moves in a circle toward a LiCoO₂ ceramic target. Sputtering is undertaken by inducing the ECR plasma to the ceramic target impressing RF power. The microwave and RF powers can be arbitrarily changed. The electric currents supplied to the coil were adjusted to meet the resonance condition. Li–Co–O film is deposited when the plasma flow, which includes Li, Co and O, collides with the substrate. Stainless steel (SUS) or quartz glasses are used as the substrates. The SUS substrates are mechanically polished to provide them with a mirror surface. Pt and Ti layers are deposited as current collectors on the quartz glasses by RF magnetron sputtering (ANELVA Corp., SPF-430H). The sputtering conditions are examined by preparing Li–Co–O films under various conditions as regards microwave power, RF power, and the argon and oxygen gas flow ratio. The obtained Li–Co–O films were identified with X-ray diffraction (XRD) analysis equipment (Rigaku Co. Ltd., RINT2100HF). An X-ray with a small incident angle of 5° was used to evaluate the thin oxide film. The thickness of the oxide films was measured by using a stylus technique (ULVAC, Inc., Dectak3030) and a scanning electron microscope (JEOL Ltd., JSM-890).

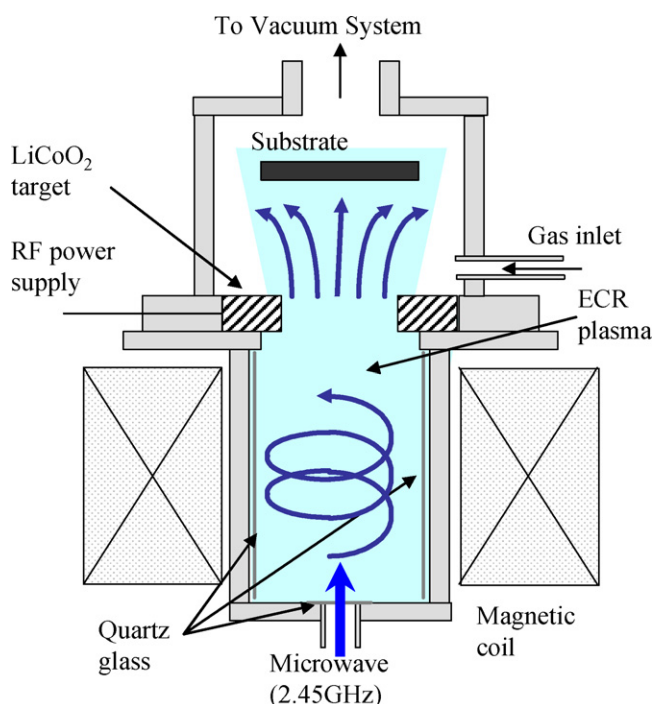


Fig. 1. Schematic illustration of ECR plasma sputtering equipment. Arrows in the chamber indicate the ECR plasma flow direction.

Electrochemical tests using the obtained film were carried out using beaker-type three-electrode cells in electrolyte solutions of 1 mol l⁻¹ LiPF₆/EC-DMC (1:1 in volume) under galvanostatic conditions. Metallic lithium was used as the counter and reference electrodes.

All-solid-state thin-film lithium batteries were prepared as described below. A lithium phosphorus oxynitride (LiPON) electrolyte film and a metallic negative lithium film were deposited on the LiCoO₂ film by RF magnetron sputtering (ANELVA Corp., SPL-210) and vacuum thermal evaporation, respectively [3]. The heat treatment was carried out at 200 °C in Ar gas to improve the contact between LiCoO₂ and LiPON. LiPON films were prepared by RF magnetron sputtering using a Li₃PO₄ target under a N₂ and Ar gas flow. The conductivities of the LiPON films deposited on comb-shaped gold microelectrodes were measured with an AC impedance analyzer (Solartron, SI1260). Finally, a copper current collector was also deposited on lithium film by the vacuum thermal evaporation method. Metal or plastic masks of various sizes were used in each process to avoid a short circuit. The resulting thin-film batteries were investigated with respect to their electrochemical properties. All the electrochemical experiments were carried out with Mac Pile II system (Bio-Logic) in a dry atmosphere at a dew point of less than -50 °C.

3. Results and discussion

Li–Co–O films were prepared by the ECR plasma sputtering method at microwave and RF powers of (a) 500, 500 W, (b) 800, 300 W, and (c) 800, 500 W, respectively, under fixed gas ratios of Ar: 20 sccm and O₂: 5 sccm. Fig. 2 shows XRD patterns of these films, indicating peak positions corresponding to

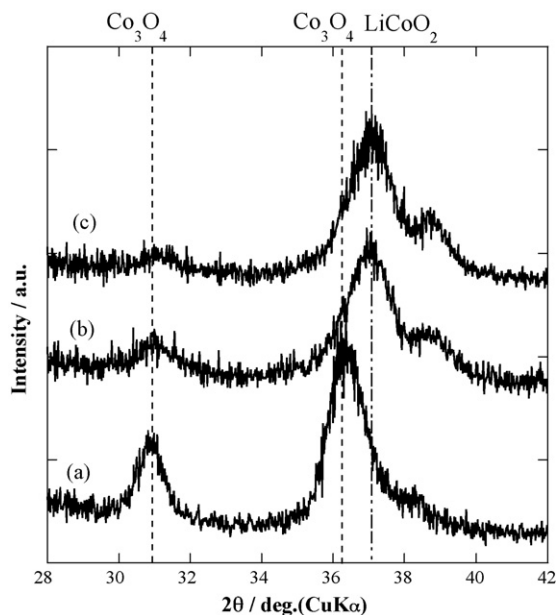


Fig. 2. XRD patterns of Li–Co–O films prepared by the ECR plasma sputtering method at microwave and RF powers of (a) 500, 500 W, (b) 800, 300 W, (c) 800, 500 W, respectively, under Ar and O₂ gas flows of 20 and 5 sccm, respectively. Sputtering time: 6 h.

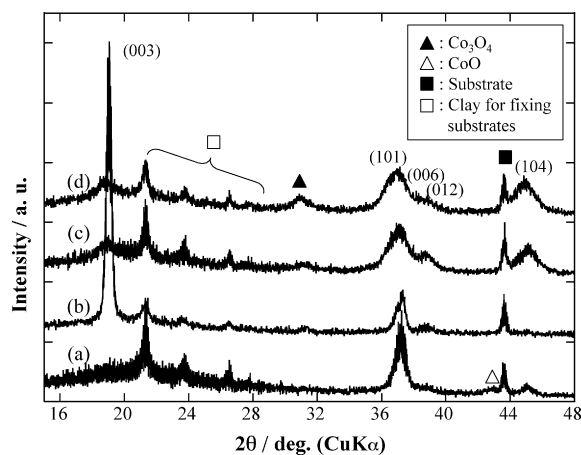


Fig. 3. XRD patterns of LiCoO₂ films prepared by ECR plasma sputtering method under the condition of microwave power: 800 W and RF power: 500 W. O₂ flow rate (sccm): (a) 0, (b) 0.5, (c) 5.0 and (d) 20. Ar flow rate (sccm): (a–d) 20. Sputtering time: (a) 3 h, (b–d) 20 h.

LiCoO₂ (JCPDS No. 50-0653) and Co₃O₄ (No. 43-1003). It is well known that Co₃O₄ coexists with LiCoO₂ because of the deficiency in the Li content in films prepared by the sputtering method [3–7]. The main phase of the film prepared at microwave and RF powers of 500 and 500 W, respectively, is identified as Co₃O₄ as shown in this figure. The peaks near $2\theta = 36^\circ$ are shifted to the 37° peak that corresponds to LiCoO₂ by increasing the microwave power, although small Co₃O₄ peaks are observed. As a result, the microwave power is an effective factor for obtaining the LiCoO₂ phase. As regards the RF power, the film deposition rate can be improved by increasing the RF power. When we compare sample (b) with sample (c), the deposition rate of the latter (8.9 nm min^{-1}) was indeed higher than that of the former (4.2 nm min^{-1}). However, the degree of crystallization of these oxide films seemed to be relatively low as the positive electrode film. Hence more precise sputtering conditions were investigated with fixed microwave and RF powers of 800 and 500 W, respectively. The LiCoO₂ films were prepared by changing the gas mixture ratio, e.g. O₂: 0, 0.5, 5, 20 sccm with a fixed Ar flow rate of 20 sccm. The pressure values of the total gas were, 0.13, 0.13, 0.15 and 0.21 Pa, respectively. Fig. 3 shows XRD patterns of as-deposited LiCoO₂ films prepared by sputtering at microwave and RF powers of 800 and 500 W, respectively, in the above mixed gas flow. At high ratios of O₂: 5 and 20 sccm, the oxide films are found to contain the LiCoO₂ phase despite the coexistence of Co₃O₄ impurities. These XRD patterns suggest that all the peaks that correspond to LiCoO₂ are rather broad, which indicates that these films are not highly crystallized. The films obtained at O₂: 5 and 20 sccm are not suitable for use as a positive electrode due to the low degree of crystallization. On the other hand, at low ratios of O₂: 0 and 0.5 sccm, the oxide films are comparatively well crystallized as indicated by their strong and sharp peaks. The film obtained at O₂: 0.5 sccm has a sharp and strong (003) peak, although the film obtained without an O₂ flow contains CoO as impurities. The preparation of LiCoO₂ films at least requires the use of plasma including oxygen to prevent reduction from Co³⁺ to Co²⁺. It is difficult to understand

the formation mechanism of the LiCoO₂ films prepared by the ECR plasma sputtering method. In a forthcoming paper, we will provide a detailed analysis of the crystal growth mechanism of LiCoO₂ films prepared in this way, which we will include how LiCoO₂ coexists with Co₃O₄. On the basis of the above results, we concluded that the LiCoO₂ film obtained at O₂: 0.5 sccm was the most appropriate for use as the positive electrode film of a thin-film battery.

Fig. 4 shows SEM images of a top view and a cross-sectional view of LiCoO₂ film prepared on an SUS substrate at O₂: 0.5 sccm, which is indicated as sample (b) in Fig. 3. The top-view image revealed that the surface of the LiCoO₂ film consisted of submicron grains and was homogeneous without large prominent grains. The LiCoO₂ film had a columnar structure with a thickness of about 6.0 μm as shown in the cross-sectional image. The oxide crystal was found to grow vertically to a thickness of less than 0.5 μm and decline slightly at a certain angle. The deposition rate of this film was estimated to be about 17 nm min^{-1} . It is well known that the deposition rates have a roughly linear relationship with the Ar to O₂ ratios when oxide film is prepared by the sputtering method [6]. A high Ar ratio of Ar:O₂ = 20:0.5 seemed to enhance the sputtering efficiency, thus allowing us to prepare thicker film. The oxide films obtained in this study have polycrystalline structures. There are a great number of grain boundaries that are composed by connecting the oxide crystallites to each other. The grain boundaries may act as barriers when Li ions diffuse in the oxide films. In a film with a columnar structure, as shown in Fig. 4(b), the electrode performance, especially with high-rate charging and discharging, would be improved by reducing the number of grain boundaries. Moreover, a positive film of micrometer order thickness would provide a larger battery capacity.

Bates et al. [3–5] reported that when they prepared LiCoO₂ films by RF magnetron sputtering, peaks corresponding to the (101) and (104) planes were clearly observed, and the (003) plane was not observed for films thicker than about 1 μm . These results are different from ours where the XRD pattern of the film with a thickness of about 6 μm has a strong and sharp (003) peak. This suggests that the growth of LiCoO₂ film by ECR plasma sputtering may involve another mechanism related to the energy and temperature of the plasma and the deposition reaction on the substrate, which are different from those of the conventional sputtering method. We consider that the ionic radiation density and the ECR plasma propagation mechanism caused the differences in the oxide crystal growth mechanism.

During the deposition process, the substrate temperature increased to about 200 $^\circ\text{C}$ with 6 h of plasma radiation without the substrate heating. Consequently, additional experiments revealed that the temperature homogeneity and deposition rate of the oxide film could be improved at substrate temperatures below 300 $^\circ\text{C}$. A heat-resistant polymer such as polyimide can be used as a flexible substrate even when the process includes heating the substrate to 300 $^\circ\text{C}$. As a result, the oxide film prepared under the substrate heating below 300 $^\circ\text{C}$ in a low O₂ flow is suitable for the positive electrode film of a thin-film battery.

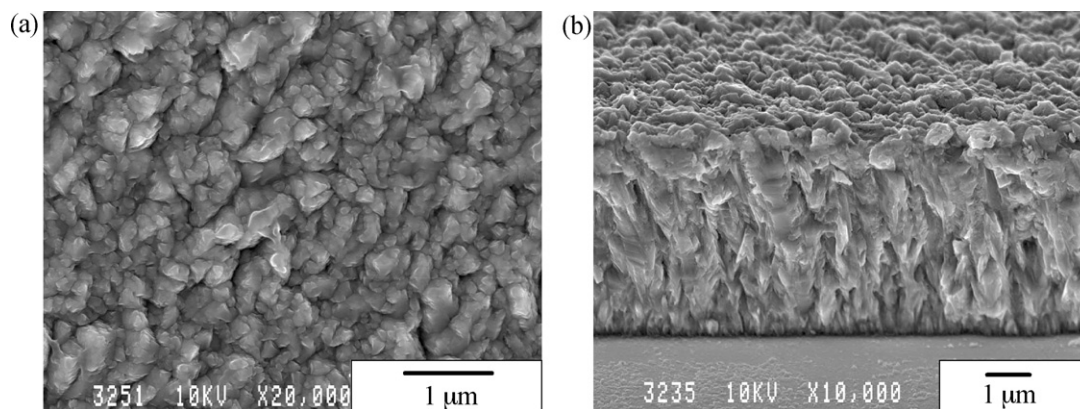


Fig. 4. SEM image of (a) top view and (b) cross-sectional view of as-deposited $\text{LiCoO}_2/\text{SUS}$ prepared by ECR plasma sputtering method.

Fig. 5 shows the electrochemical performance of samples (b) and (c) shown in Fig. 3 in electrolyte solutions with a current density of $20 \mu\text{A cm}^{-2}$. In this figure, samples (b) and (c) are denoted as LCO1 and LCO2, respectively. The film

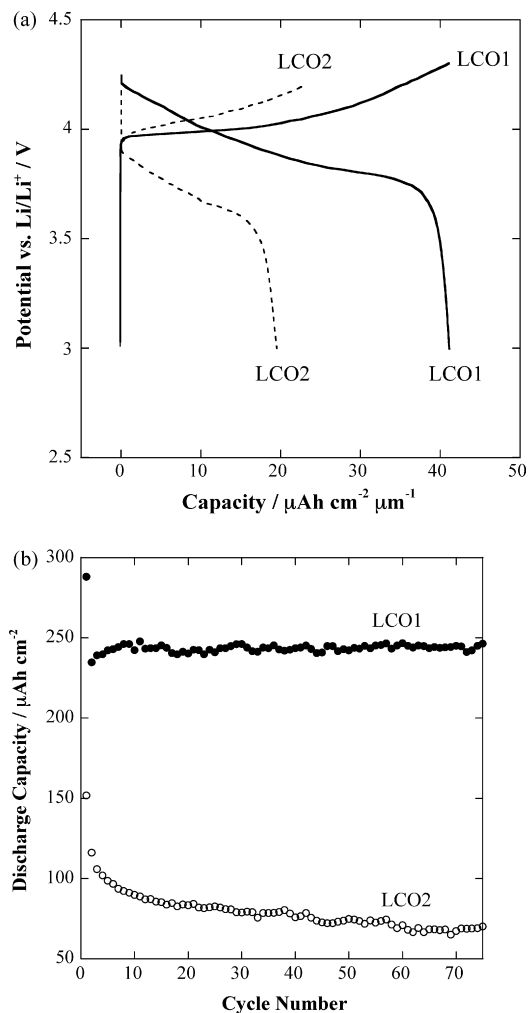


Fig. 5. Electrochemical properties of (a) charge and discharge curves at 75th cycle and (b) cycle performance of LiCoO_2 films prepared by ECR sputtering method in an electrolyte solution of $1 \text{ mol l}^{-1} \text{LiPF}_6/\text{EC-DMC}$ under a galvanostatic condition of $20 \mu\text{A cm}^{-2}$. LCO1 and LCO2 indicate sample (b) and sample (c) as shown in Fig. 3, respectively.

thicknesses of LCO1 and LCO2 were 6.0 and $3.3 \mu\text{m}$, respectively. The charge and discharge capacities were normalized by the film thickness for comparison. LCO1 exhibited a larger capacity and smaller overpotential than LCO2 as shown in Fig. 5(a). Moreover LCO1 exhibited a superior cycle property to LCO2 as shown in Fig. 5(b). LCO1 is found to have higher crystallinity than LCO2 from the XRD patterns. These results indicate that the high crystallinity of the LiCoO_2 film contributes to the good electrochemical performance, and the film will be suitable for use as the positive electrode of an all-solid-state thin-film battery. However, the specific capacity of about $40 \mu\text{A cm}^{-2} \mu\text{m}^{-1}$ for LCO1 is rather low compared with the theoretical specific capacity of $69 \mu\text{A cm}^{-2} \mu\text{m}^{-1}$ because of the existence of Co_3O_4 impurities and the comparatively low densities of the oxide films. The specific capacity of LiCoO_2 film would be improved by reducing the impurity content and growing oxide crystals with higher packing density under the more precisely controlled sputtering conditions.

Fig. 6 shows the temperature dependence of the conductivity of LiPON films deposited in a N_2 and Ar gas flow. The conductivity is improved by increasing the N_2 content of the flow. A LiPON film deposited in a pure N_2 flow has the highest con-

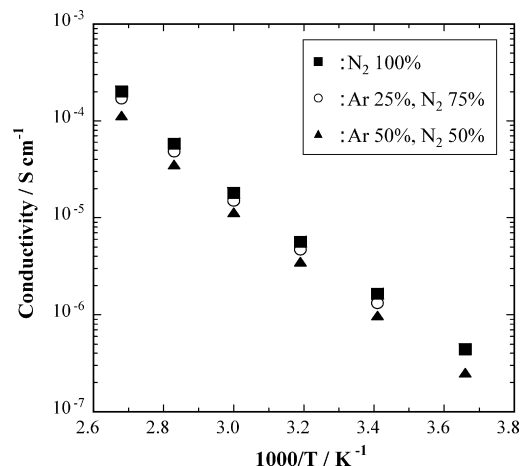


Fig. 6. Temperature dependence of conductivities of LiPON films deposited in a $\text{N}_2 + \text{Ar}$ gas flow.

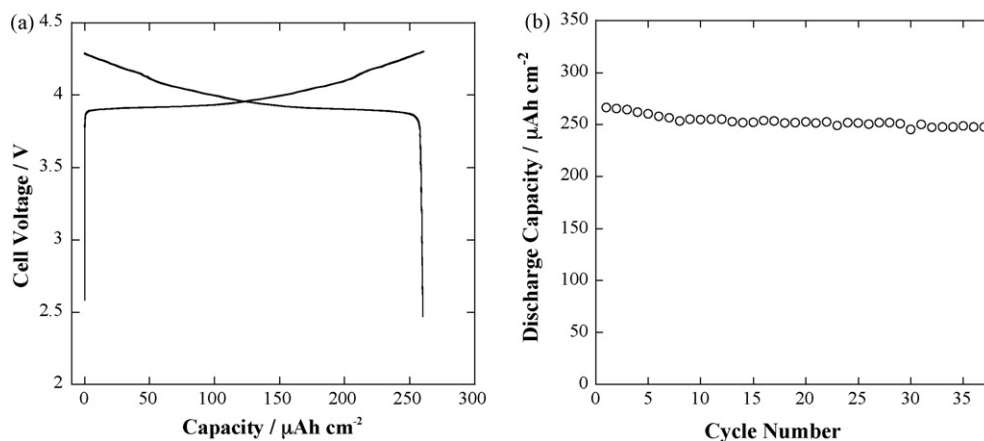


Fig. 7. Electrochemical properties of an all-solid-state thin-film lithium battery using positive LiCoO_2 film prepared by the ECR sputtering method under a galvanostatic condition of $20 \mu\text{A cm}^{-2}$; (a) Charge and discharge curves at 5th cycle and (b) cycle performance.

ductivity of $\mu\text{S cm}^{-1}$ order at room temperature. This value is consistent with previous reports [3–5].

All-solid-state thin-film lithium batteries were fabricated by depositing LiPON, lithium and copper in sequence on a LiCoO_2 film. Here the LiCoO_2 film was prepared by keeping the substrate temperature at 300°C under the same power and gas flow conditions as those used for sample (b) in Fig. 3, and with Pt/Ti/quartz glass as the substrate. The XRD pattern of the LiCoO_2 film was almost the same as the pattern obtained without heating the substrate. The LiPON film was deposited in a pure N_2 flow by RF magnetron sputtering. The oxide film was $6.2 \mu\text{m}$ thick. The total thickness excluding the Pt/Ti/quartz substrate, and the effective surface area of this battery were about $10 \mu\text{m}$ and 0.48 cm^2 , respectively. Fig. 7(a) shows a charge–discharge curve for the fifth cycle under a galvanostatic condition of $20 \mu\text{A cm}^{-2}$ in the 4.3–2.5 V voltage range. The cycling performance of this cell is shown in Fig. 7(b). As shown in this figure, plateaus were observed near 3.9 V in the charging, and discharging processes and both capacities had almost the same value. This behavior is consistent with previous reports [3–6]. Moreover the discharge capacities shown in Fig. 7 have almost the same values as those measured in the electrolyte solution shown in Fig. 5. This indicates that as-deposited LiCoO_2 film can function as a positive electrode regardless of the film thickness of about $6 \mu\text{m}$, and the interfaces of both $\text{LiCoO}_2/\text{LiPON}$ and LiPON/Li are electrochemically intact to form the path for the Li-ion diffusion. The thin-film battery exhibited a discharge capacity of about $250 \mu\text{Ah cm}^{-2}$, and the energy density was estimated to be about 1 mWh cm^{-2} . The cell in this study had a rather large energy density yet reported. Furthermore this cell exhibited a stable cycle performance as shown in Fig. 7(b).

Fig. 8 shows the discharge curves of an all-solid-state thin-film lithium battery under a galvanostatic condition of various current densities. The downward shift of the curves to a lower voltage and the decrease in the battery capacities were caused by the cell resistance. However, this battery exhibits high discharge capacities of more than $100 \mu\text{Ah cm}^{-2}$ at high current densities of mA cm^{-2} order. The rapid decrease in the cell voltage would

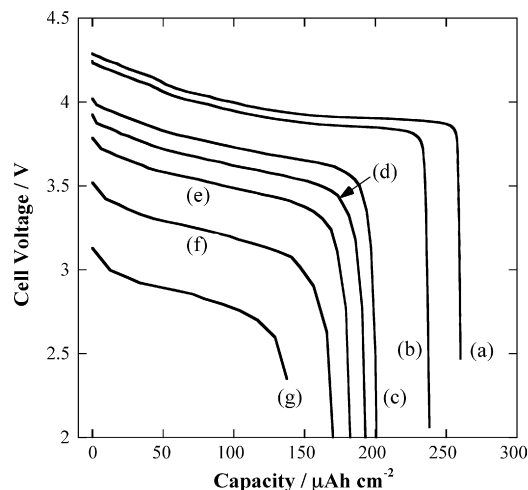


Fig. 8. Discharge curves of an all-solid-state thin-film lithium battery under a galvanostatic condition of (a) 0.02, (b) 0.2, (c) 1.0, (d) 1.5, (e) 2.0, (f) 3.0 and (g) 4.0 mA cm^{-2} .

be avoided by improving the interface contact of each electrode film.

4. Conclusions

The conditions for depositing of LiCoO_2 films by the ECR plasma sputtering method were investigated as regards microwave power, RF power, gas flow composition and substrate temperature. Of these parameters, the O_2 to Ar ratio was very important in terms of obtaining well-crystallized LiCoO_2 films without a post-annealing process. All-solid-state thin-film lithium batteries, prepared by depositing LiPON and metallic lithium on the as-deposited LiCoO_2 films with a thickness of $6.2 \mu\text{m}$, exhibited a rather large energy density of about 1 mWh cm^{-2} and a stable cycle performance. The batteries showed good properties even at high current densities. Based on the results obtained in this study, we consider that the ECR plasma sputtering method offers the great advantage of enabling us to prepare well-crystallized oxide films using a low-

temperature process. The ECR plasma sputtering method is a promising candidate for preparing high-performance positive electrodes at a lower cost without the need for a post-annealing process. Moreover, we revealed the feasibility of preparing thin-film batteries on flexible polymer substrates without the post-annealing process by using the ECR plasma sputtering method.

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References

- [1] J. Yamaki, H. Ohtsuka, T. Shodai, *Solid State Ionics* 86–88 (1996) 1279.
- [2] H. Ohtsuka, Y. Sakurai, *Solid State Ionics* 144 (2001) 59.
- [3] J.B. Bates, N.J. Dudney, B.J. Neudecker, F.X. Hart, H.P. Jun, S.A. Hackney, *J. Electrochem. Soc.* 147 (2000) 59.
- [4] J.B. Bates, N.J. Dudney, B. Neudecker, A. Ueda, C.D. Evans, *Solid State Ionics* 135 (2000) 33.
- [5] X. Yu, J.B. Bates, G.E. Jellison, *J. Electrochem. Soc.* 144 (1997) 524.
- [6] J.F. Whitacre, W.C. West, E. Brandon, B.V. Ratnakumar, *J. Electrochem. Soc.* 148 (2001) A1078.
- [7] Cheng-Lung Liao, Kuan-Zong Fung, *J. Power Sources* 128 (2004) 263.
- [8] H. Xia, L. Lu, G. Ceder, *J. Power Sources* 159 (2006) 1422.
- [9] Y. Iriyama, M. Inaba, T. Abe, Z. Ogumi, *J. Power Sources* 94 (2001) 175.
- [10] Y. Iriyama, H. Kurita, I. Yamada, T. Abe, Z. Ogumi, *J. Power Sources* 137 (2004) 111.
- [11] Y.H. Rho, K. Kanamura, T. Umegaki, *J. Electrochem. Soc.* 150 (2003) A107.
- [12] S. Hirono, S. Umemura, M. Tomita, R. Kaneko, *Appl. Phys. Lett.* 80 (2002) 425.