Short communication

Preparation and performances of highly porous layered LiCoO$_2$ films for lithium batteries

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Abstract

Layered lithium cobalt oxide (LiCoO$_2$) cathode films were successfully deposited onto an aluminum substrate with a large surface area by electrostatic spray deposition (ESD). Highly porous films were prepared by ESD using cobalt acetate tetrahydrate (CoOAc) and lithium hydroxide monohydrate (LiOH) dissolved ethyl alcohol (15 vol.%) and di(ethylene glycol)butyl ether (85 vol.%) as a precursor solution. An LiCoO$_2$ film, the crystal structure of which contained a combination of layered and spinel regions, was synthesized by heat treatment for 2 h at 400 °C. Charge–discharge curves showed that the capacity of this film was 120 mAh g^{-1}. Heat treatment at 650 °C was shown to be a low enough temperature for the resulting film to be used with an aluminum substrate and to allow the retention of the morphology of the surface on which the film is deposited. The discharge capacity for the layered LiCoO$_2$ region of this film was 140 mA g^{-1} at a rate of 1C and it achieved a good cycle and a rate performance without the need for auxiliary materials.
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Keywords: Layered lithium cobalt oxide; Electrostatic spray deposition; Lithium ion batteries; Cathode films; Crystalline structures

1. Introduction

The development of high power lithium ion batteries is required for applications in microbatteries, power tools and hybrid electric vehicles (HEVs). The improvement of manufacturing processes to reduce the need for binder and conductive auxiliary materials in these batteries is a goal of current research.

Electrostatic spray deposition (ESD) is a unique method of film formation, initially developed by Schoonman and co-workers [1]. ESD makes possible the preparation of a cathode film without the use of extra binder and conductive materials. The structures of lithium films, and hence their electrochemical properties, are controllable by varying the deposit conditions, allowing the creation of dense or porous film, with pore and wall sizes ranging from below 1 μm to over 10 μm [2].

Lithium cobalt oxide (LiCoO$_2$) is the basic and most reliable cathode material used in lithium ion batteries. Various methods have been used in the attempts to prepare cathode films using nanotechnology. These include pulsed laser deposition (LPD) [3–5], sputter deposition [6–9], electrophoretic deposition [10],

chemical vapor deposition (CVD) [11,12], sol–gel [13,14] and template methods [15,16], as well as ESD [2,17–21]. ESD is the only way to direct thick cathode film fabrication method on current corrector.

LiCoO$_2$ exhibits two distinct crystal structures. These are layered LiCoO$_2$, usually synthesized at temperatures of over 700 °C to produce a hexagonal layered structure, and lithiated-spinel Li$_2$[Co$_2$]O$_4$, usually synthesized at low temperatures of around 400 °C to generate a cubic spinel-related structure [22]. Layered LiCoO$_2$, which is more suitable for lithium ion batteries than lithiated-spinel LiCoO$_2$, is usually calcinated at 850–900 °C in solid state reaction. The high temperature required during synthesis means that a costly platinum or gold substrate is required for directly film formation method on current corrector, as the temperature exceeds the melting point of aluminum (660 °C) which is usual current corrector for cathode. The methods of physical depositions, such as sputter deposition and LPD do not require heat treatment but have been shown to achieve only a low deposition rate and previous trials have managed to produce only a dense surface structure unless combined with a lithographic method. Although several of the chemical and physical methods have displayed useful characteristics, these have not been sufficient for practical use, as low rates of film formation, the necessity for untenably high calcination temperatures and the

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restricted surface area covered would result in unfeasibly high costs of fabrication.

In comparison, ESD provides a promising method for applying the films a large surface area with high rate and low cost. Many efforts have been developed to prepare $LiCoO_2$ by ESD. Various surface structures were obtained by controlling spray conditions such as substrate temperature, spraying rate and precursor concentrations [2,19–21]. However, the most common solution has so far been to use platinum, gold or stainless steel substrates to allow high-temperature heat treatments.

In this study, layered $LiCoO_2$ films without binder and conductive additives were applied to an aluminum substrate, at limited heat treatment temperature, with a relatively large surface area using ESD. The surface morphology, crystalline structure and the electrochemical properties required for use as the cathode of lithium ion batteries, such as discharge capacity, rechargeability and cycle performances, were investigated with reference to the conditions of film preparation.

2. Experimental

$LiCoO_2$ cathode films were prepared by ESD with a downward spraying setup [20] using lithium hydroxide monohydrate (LiOH) as a lithium source and cobalt acetate tetrahydrate (CoOAc) as a cobalt source (Wako Pure Chemical Industries Ltd.). These source materials were dissolved in mixed solvent of ethanol (15 vol.%) and di(ethylene glycol)butyl ether (85 vol.%; Wako Pure Chemical Industries Ltd.) of $0.005 \, mol \, dm^{-3}$ concentration each.

Using by liquid-delivered ESD, the cathode films were deposited on aluminum disk substrate (13 mm in diameter) mounted on a stainless steel block heated to 240 °C. A capillary nozzle was connected to the pump to deliver the precursor solution at a rate of $0.5 \, ml \, h^{-1}$ at a distance of 15 mm from the substrate. A positive high voltage (3–5 kV) was applied between the nozzle and the substrate in the corn-jet mode [23]. Ejected precursor solutions were atomized at the end of the nozzle before moving toward the heated substrate. Cathode films were formed on the substrate by the thermal decomposition of the precursor solutions. The films were heat treated for crystallization for 2 h at 400 °C to yield low temperature-$LiCoO_2$ (LT-$LiCoO_2$) or 650 °C to yield high temperature-$LiCoO_2$ (HT-$LiCoO_2$).

Surface morphologies and crystal structures of the films were investigated by scanning electron microscopy (SEM;

JSM-6700F, JEOL Ltd.), X-ray diffraction (XRD; RINT 2000, Rigaku Corp.) and Raman spectroscopy (HoloLab 5000, Kaiser Optical Systems Inc.). Electrochemical performances, Charge–discharge tests, were measured by the construction of coin-type cells. The cells were assembled using the heat-treated films as cathodes, lithium metal (Honjo Metal Co.) as an anode and a $1 \, mol \, dm^{-3}$ of lithium hexafluorophosphate containing a solution of ethylenecarbonate (50 vol.%) and diethylcarbonate (50 vol.%) as an electrolyte (Tomiyama Pure Chemical Industries Ltd.). Charge–discharge tests ware carried out using a computer-controlled potentiostat (HJ–101SM6, Hokuto Denko Corp.) with a potential range of between 3.0 or 3.5 and 4.2 V.

3. Results and discussion

LiOH was selected as the lithium source based on the results of a previous study. Lithium acetate is known to yield porous $LiCoO_2$ films but sometime melt down the porous structure during heat treatment because of its low melting point, 286 °C. On the other hand, it was shown that LiOH gave a porous surface structure in the case of the synthesis of lithium manganese oxide even if a high temperature heat treatment [24]. Fig. 1 shows an SEM image of the typical surface morphology of a $LiCoO_2$ film prepared by ESD and after heat treatment at 650 °C for 2 h. Walls measuring a few micrometers and holes of approximately 5 μm diameters were observed. The same morphology was observed in films that were heat treated at 400 °C for 2 h.

The crystal structures of the films were investigated by XRD (Fig. 2) [25,26]. Prepared film heat treated at 240 °C showed no peak (data not shown) but $LiCoO_2$ crystal structure phases were observed after heat treatment at a temperature of more than 400 °C for 2 h. The pattern of LT-$LiCoO_2$, heat treated at 400 °C, was indexed to the lithiated-spinel $Li_2[Co_2]O_4$ structure with the space group $Fd3m$. HT-$LiCoO_2$ film, heat treated at 650 °C for 2 h, indexed to the layered $LiCoO_2$ structure with space group $R\bar{3}m$. Expansion of around 19° and 66° 2θ for both LT and HT-$LiCoO_2$ is shown in Fig. 3. LT-$LiCoO_2$ has the possibility to have two peaks related with lithiated-spinel $Li_2[Co_2]O_4$ and layered $LiCoO_2$ around 19° but it is difficult to find peaks for layered $LiCoO_2$ around 66° 2θ. In any case, the quality of XRD patterns is insufficient to distinguish the minor component of layered $LiCoO_2$ from the dominant lithiated-spinel phase, as would be possible using film analyses.
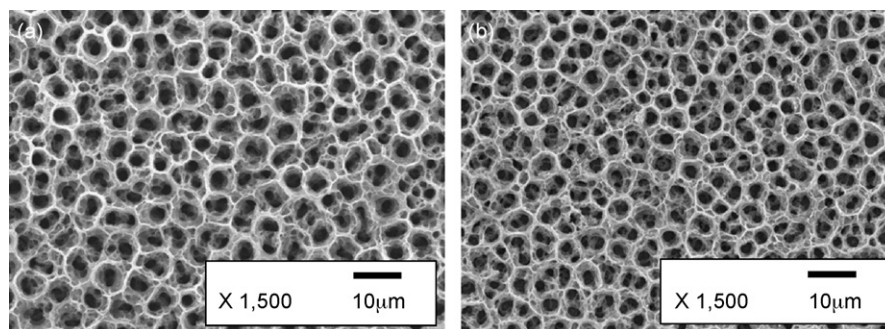

Fig. 1. SEM images of surface morphologies of $LiCoO_2$ films prepared by ESD. (a) As prepared and (b) after heat treated at 650 °C for 2 h.
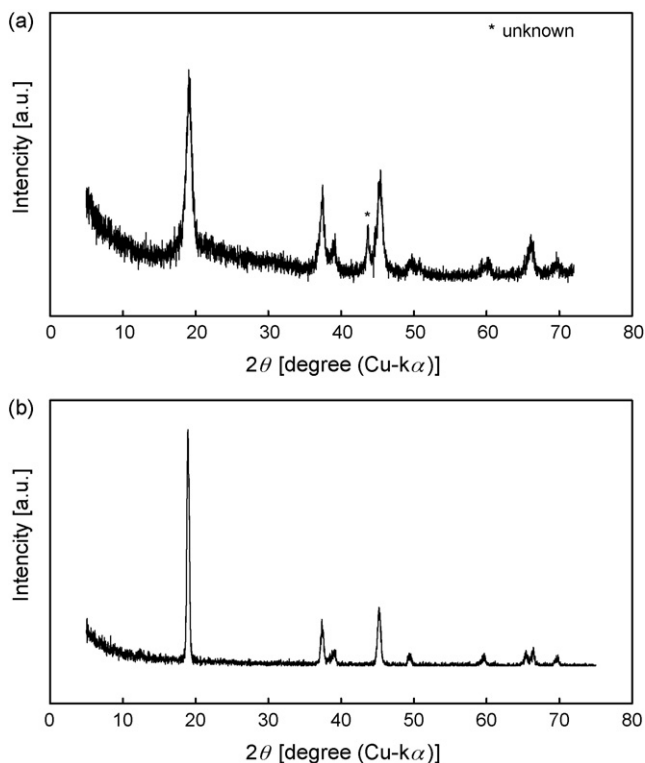
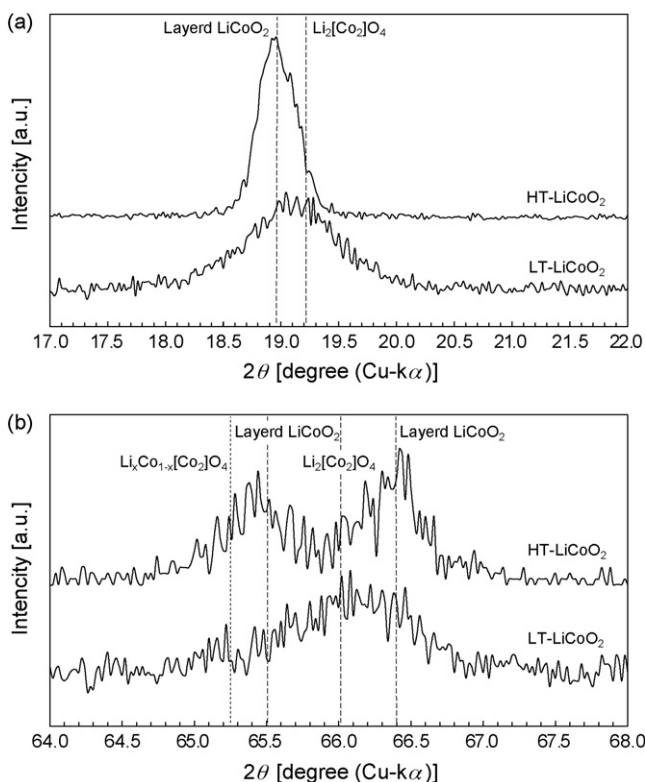Fig. 2. XRD patterns of $LiCoO_2$ films prepared by ESD heat treated 2 h for (a) 400 °C and (b) 650 °C.

Table 1
Raman shift of the layered $LiCoO_2$ and lithiated-spinel $Li_2[Co_2]O_4$

Component	Raman shift [cm^{-1}]
Lithiated-spinel $Li_2[Co_2]O_4$	603, 587, 482, 447
Layered $LiCoO_2$	595, 486

A Raman scattering spectrum is a useful tool for investigating the crystalline structure of lithium films because it can detect signals only a few micrometers from the surface. Table 1 shows the Raman peaks of lithiated-spinel $Li_2[Co_2]O_4$ and layered $LiCoO_2$ reported by Huang and Frech [27], and spinel phase coexists with layered $LiTi_{0.25}Co_{0.75}O_2$ appeared by Gopukumar et al. [28]. Fig. 4 shows the Raman scattering spectra of our heat-treated films. Four peaks were observed located at frequencies of 607, 592, 487 and 452 cm^{-1} in LT-$LiCoO_2$. These peak positions close to lithiated-spinel $Li_2[Co_2]O_4$ found in the literature but the peak height ratio is completely another. The peak positions of $LiTi_{0.25}Co_{0.75}O_2$ are also located almost same to the lithiated-spinel $Li_2[Co_2]O_4$ but the height ratio is difference. It should consider to coexistence lithiated-spinel $Li_2[Co_2]O_4$ and layered $LiCoO_2$ phase in the LT-$LiCoO_2$ because which peak positions and height ratio are quite similar to the $LiTi_{0.25}Co_{0.75}O_2$.

Horn et al. reported that the layered $LiCoO_2$ phase formed at 400 °C for several days after solid-state reaction [25]. In contrast, this phase was formed only a few hours of heat treatment at 400 °C when our films were prepared by ESD. This demonstrates that a short period of heat treatment is sufficient when
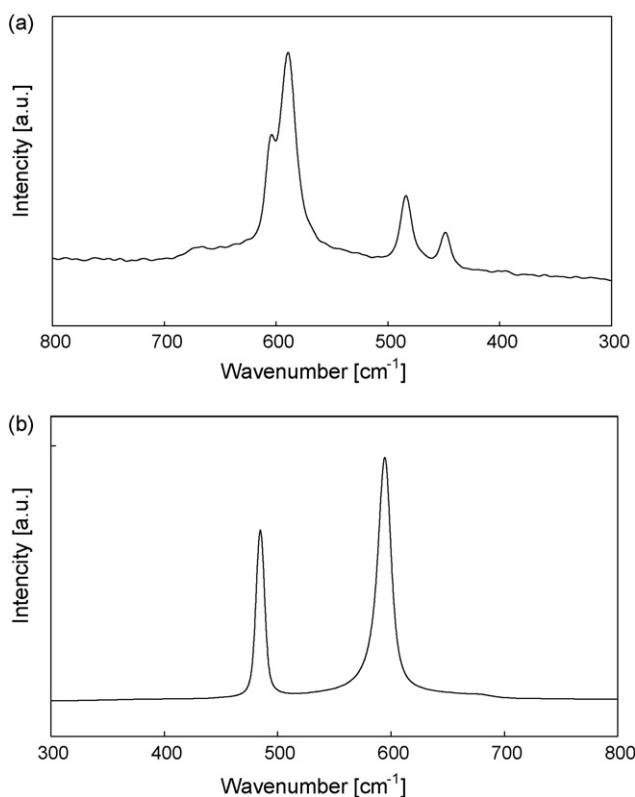

Fig. 3. Expansion of XRD patterns $LiCoO_2$ films prepared by ESD heat treated 2 h for 400 and 650 °C near (a) 19° 2θ and (b) 66° 2θ.

Fig. 4. Raman scattering spectra of $LiCoO_2$ films prepared by ESD heat treated 2 h for (a) 400 °C and (b) 650 °C.
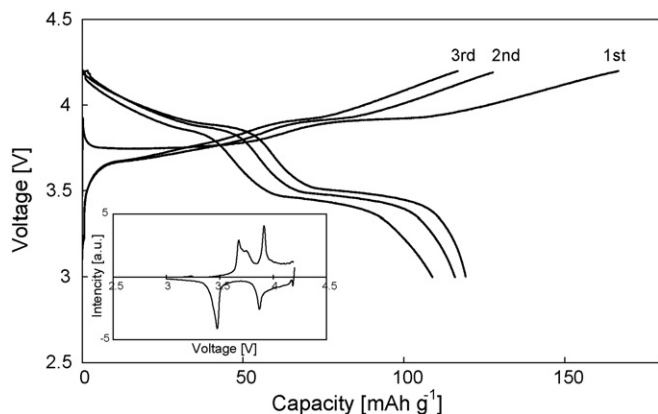
Fig. 5. Charge–discharge curves of the first three cycles of LT-LiCoO$_2$ film from 3 to 4.2 V at 1C rate and differential curve of the second cycle.

the LiCoO$_2$ synthesized is derived from a well-mixed solute source. The Raman scattering spectra of HT-LiCoO$_2$ exhibits a single phase of layered LiCoO$_2$, reaching peaks of 486 cm^{-1} (E_g), 596 cm^{-1} (A_{1g}) and practically nought Co$_3$O$_4$ (686 cm^{-1}).

The electrochemical performances of the films in the absence of binder and conductive materials were investigated. Fig. 5 shows the charge–discharge curves of the first three cycles of LT-LiCoO$_2$ from 3 to 4.2 V at a rate of 1C and a differential curve of the second cycle. The capacity of the first cycle is 120 mAh g^{-1}, and the charge–discharge curves have two plateaus, while the corresponding two pairs of peaks appear as differential curves. The first peak of the differential charge curve is slightly collapsed but the two pairs of peaks fit with those reported for lithiated-spinel Li$_2$[Co$_2$]O$_4$ and layered LiCoO$_2$ [29]. This provides further evidence for the formation of layered LiCoO$_2$ by heat treatment at 400 °C for 2 h. The first cycle has a large irreversible capacity. Thereafter, the discharge capacity decreased with each successive cycle, reaching about a half of the original capacity after the 10th cycle (not shown). LT-LiCoO$_2$ is not suited for the cathode of the lithium batteries.

Fig. 6 shows the charge–discharge curves of the first three cycles of HT-LiCoO$_2$ from 3.5 to 4.2 V at a rate of 1C. The differential curve of the second cycle is also shown. These
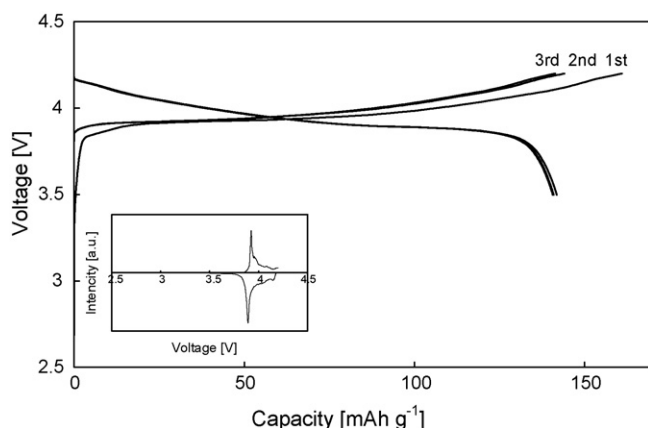

Fig. 6. Charge–discharge curves of the first three cycles of HT-LiCoO$_2$ film from 3.5 to 4.2 V at 1C rate and differential curve of the second cycle.
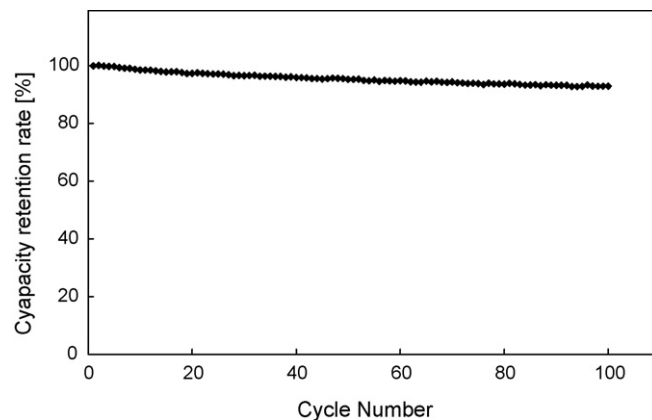

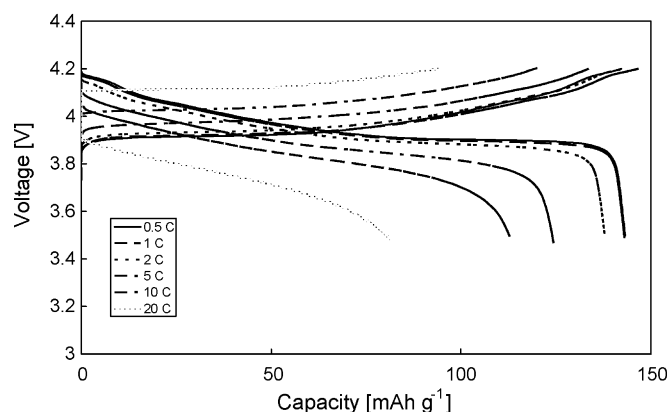Fig. 7. Cycle performance of HT-LiCoO$_2$ film at 1C rate.

Fig. 8. Rate performances of HT-LiCoO$_2$ film.

charge–discharge curves have only one plateau and the differential curve peaks corresponding to layered LiCoO$_2$ [29]. Only the first cycle has about 10% of irreversible capacity, which is difference between charged capacity and discharged capacity, but almost 100% charge–discharge efficiency is retained in the second and subsequent cycles. The capacity of the first cycle is 140 mAh g^{-1}. Fig. 7 shows the cycle performance at a rate of 1C. The capacity after 100 cycles is still 93% of that of the first cycle. Fig. 8 shows the rate performance of the film. The capacity did not diminish up to 1 °C and it is kept 79 and 57% at 10 and 20C, respectively. Charge–discharge curves just sifted high or low voltage caused by ohmic resistance but the lithium intercalation and deintercalation are still smooth in case of high rate. This demonstrates that a cathode film prepared by ESD with heat treatment at 650 °C can achieve a capacity close to the theoretically and its works long cycling and high rate use although no binder and conductive additives.

4. Conclusions

Using ESD, layered LiCoO$_2$ can be formed through heat treatment at a relatively low temperature of 400 °C in the comparatively short period of 2 h. While the layered phase is mixed with the lithiated-spinel phase, our results demonstrate the potential for low-temperature synthesis of layered LiCoO$_2$.

Further, we have shown that heat treatment at high temperatures below 650 °C yields single layered LiCoO$_2$ for direct film formation on aluminium substrate using the ESD. The film displays excellent capacity, cycle and rate performance, even in the absence of binder and conductive additives.

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