

Synthesis and Electrode properties of
Thick (104)-Oriented LiCoO₂ Epitaxial Films

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Lithium-ion batteries are powering most of today's portable electronics and have come to be enlarged and installed in hybrid and electric vehicles. On the other hand, there are also increasing demands for microbatteries including thin-film batteries to be used in microdevices such as MEMS and drug delivery systems. In thin film batteries, thick electrodes are necessary for achieving high capacity within a limited footprint. However, the increasing thickness usually lowers the rate capability; one of the dominant rate-determining factors is the grain boundary resistance. One way to overcome this problem is forming active material layer without grain boundaries, which will be achieved by epitaxial growth of the active material. In this study, LiCoO₂ was selected as a typical cathode material, and thick epitaxial films were synthesized. Metallic Nb 0.5wt%:SrTiO₃ (100) wafer was selected as the substrate to control film orientation and investigate the electrode performances.

We have previously fabricated epitaxial LiCoO₂ thin films by pulsed laser deposition (PLD) and obtained high quality epitaxial thin films on sapphire substrate by adjusting film growth conditions such as fluence and oxygen pressure (P_{O_2})^{1,2}. However, the deposition rate under the conditions², where a KrF excimer laser operated at 10 Hz of repetition rate gave fluence of 0.37 J·cm⁻² on a Li-enriched target (Li_{1.1}CoO_{2+δ}) under 0.1 Pa of P_{O_2} , was only 0.039 Å·s⁻¹. In order to increase the film deposition rate, deposition parameters were modified: the fluence and laser repetition rate rose to 0.65 J·cm⁻² and 40 Hz, respectively. Additionally, more Li-enriched target (Li_{1.2}CoO_{2+δ}) was utilized to compensate for the Li deficiency in the epitaxial films, because higher laser fluence causes more lithium loss in the ablation process. These parameters give 30 times higher deposition rate of 1.2 Å·s⁻¹ than previous conditions, then it enables the deposition of micron-order-thick LiCoO₂ epitaxial films.

Figure 1 (a) and (b) shows XRD patterns of 1 μm^t LiCoO₂ epitaxial film. LiCoO₂ 104 diffraction is detected in the out-of-plane XRD pattern, as shown in Fig.1 (a). On the other hand, the in-plane XRD pattern indicates that both of <110>_{LiCoO₂} and <018>_{LiCoO₂} are parallel to <110>_{Nb:SrTiO₃} direction. These results reveal that the film is grown with the orientation relationship shown in Fig.1 (c). This epitaxial relationship is explainable by the structural similarity between LiCoO₂ and SrTiO₃. LiCoO₂ has a layered rock salt structure ($R\bar{3}m$), where Li and Co are ordered in the cation sites among a face-centered-cubic oxygen array to form alternate Li and Co layers along the [111] direction in the NaCl-type cubic lattice. On the other hand, SrTiO₃ has a cubic perovskite structure.

Since the perovskite structure is very similar in the oxygen arrangement to the NaCl-type structure, the LiCoO₂ film on SrTiO₃ has cube-on-cube relationship illustrated in Fig.1 (c).

All-solid-state cell was fabricated in order to investigate the electrode performance. Powder Li_{3.25}Ge_{0.25}P_{0.75}S₄ (thio-LISICON) was used as the solid electrolyte. In-Li alloy was utilized as the counter electrode. Li₃PO₄ thin film was deposited by PLD on the LiCoO₂ epitaxial film in order to suppress the formation of a highly-resistive space-charge layer at the interface between LiCoO₂ and sulfide electrolyte³. They were pressed together at 500 MPa into a three-layered pellet with 10 mm diameter. Rate capability was investigated for the 10 nm^t Li₃PO₄ thin film coated 1 μm-thick LiCoO₂ film at room temperature. LiCoO₂ film was charged up to 3.58 V at 0.01 C rate, because electrode potential of the In-Li alloy counter electrodes is 0.62 V vs. Li⁺/Li, which is corresponding to charging up to Li_{0.5}CoO₂. Fig. 2 shows the discharging curves at various discharging rate.

References

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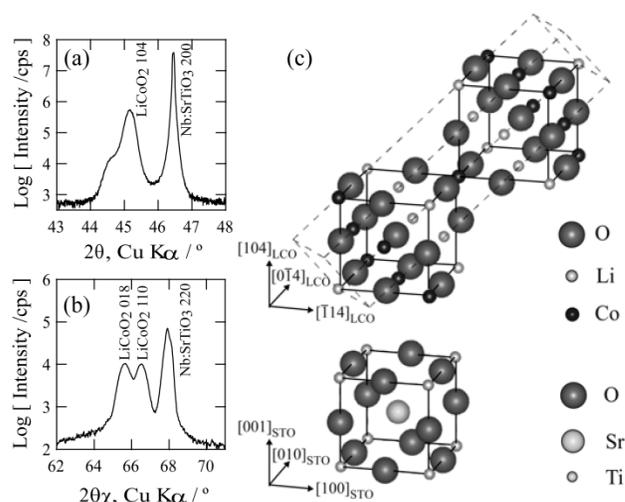


Fig.1. XRD patterns of 1 μm^t LiCoO₂ film for out of plane (a), and in-plane (b). (c) Orientation relationship between LiCoO₂ and SrTiO₃.

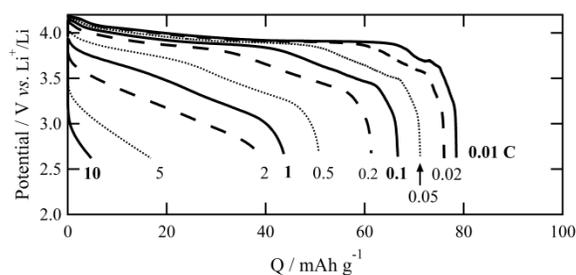


Fig.2. Rate capability of 1 μm^t LiCoO₂ epitaxial film electrode in all-solid-state battery.