Preparation of $LiCoO_2$ Epitaxial Films on Single Crystal Substrates by Sol-Gel Method

Taeri Kwon[1)], Tsuyoshi Ohnishi[1,2)], Kazunori Takada[1,2)*]
[1)] Battery Materials Unit, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan
[2)] International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

All-solid-state Li-ion battery is considered highly safe due to the use of a non-flammable ceramic solid electrolyte. However, its low current drain has been hindering the practical use. Although low ionic conductivity of solid electrolytes had been the reason for the low rate capability, rather high ionic conductivity of the order of 10^{-2} S·cm^{-1} has been recently achieved in a solid electrolyte [1]. On the other hand, because materials for solid-state batteries are usually polycrystalline, grain boundaries tend to block the ion conduction and determine the reaction rate as well; such grain boundary effects will be minimized in single-crystal materials. Such single crystals can be obtained, for example, by epitaxial growth through evaporation methods, such as vacuum evaporation, radio frequency (RF) sputtering and pulsed laser deposition (PLD). Although they have offered epitaxial films of battery materials having high crystallinity [2, 3], such evaporation methods are not suitable for mass production. In this study, we are developing a wet process that allows mass production of epitaxial $LiCoO_2$ films. Recently, we have succeeded in synthesizing $LiCoO_2$ epitaxial film onto single crystal by the growth based on a wet process.

Single-crystal $SrTiO_3$ (111), (110), and (100) substrates with dimensions of 7.5 × 7.5 × 0.5 mm^3 were used for the epitaxial growth of the $LiCoO_2$ films by the sol-gel method. An epitaxial $LiCoO_2$ film was also grown on Nb 0.5 wt%: $SrTiO_3$ (100) substrate, which acts as a conducting substrate in the electrochemical measurement. The precursor solution was an aqueous solution of lithium nitrate and cobalt nitrate with poly vinylpyroolidone (PVP) as a thickener. The precursor solution was applied to the substrates by spin coating. After the coating, the film was dried and finally heated at 700 ˚C for 5 h. The thicknesses of the films were measured with a surface profiler. Crystal orientations in the $LiCoO_2$ films were investigated by X-ray pole figure measurement. Electrode properties of the film were investigated in a solid-state cell. Surface of the $LiCoO_2$ film was coated with 10 nm-thick Li_3PO_4 film formed by pulsed laser deposition before embedding in the cell, and $Li_{3.25}Ge_{0.25}P_{0.75}S_4$ was used as the solid electrolyte. The details of the cell construction method were reported in Ref. [4].

Figure 1 shows X-ray pole figures for the 003 reflections of the $LiCoO_2$ films grown on the substrates. The poles appear as spots in all the figures, indicating that the films are epitaxially grown on the substrates. The differences in the figures reveal that the $LiCoO_2$ films are grown on the different planes of the $SrTiO_3$ with different orientations; the *c*-axes of the $LiCoO_2$ films make angles of 90˚, 55˚, and 35˚ with the surface of $SrTiO_3$ (111), (110), and (100) substrates, respectively.

Because *c*-axis of the $LiCoO_2$ film is the most inclined on $SrTiO_3$ (100), a film for the electrochemical measurement was prepared on Nb 0.5 wt%: $SrTiO_3$ (100). The film indeed shows redox reactions around 4 V vs. Li^+/Li, and the initial charge capacity at 0.01 C is 85 mAh·g^{-1} for a 70 nm-thick epitaxial $LiCoO_2$ film, while the following discharge capacity is 55 mAh·g^{-1}.

In summary, we have succeeded in the epitaxial growth of $LiCoO_2$ films with different orientations on different crystal faces of single-crystal $SrTiO_3$ substrates by the sol-gel method.

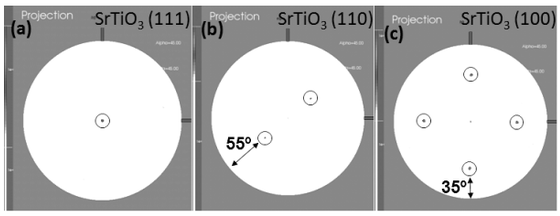

Figure 1 X-ray pole figures for 003 reflections of $LiCoO_2$ films grown on (a) $SrTiO_3$ (111), (b) $SrTiO_3$ (110), and (c) $SrTiO_3$ (100) substrates. The spots from the poles are marked with circles. (The center spot in Figure 1 (c) is caused by surface reflection.)

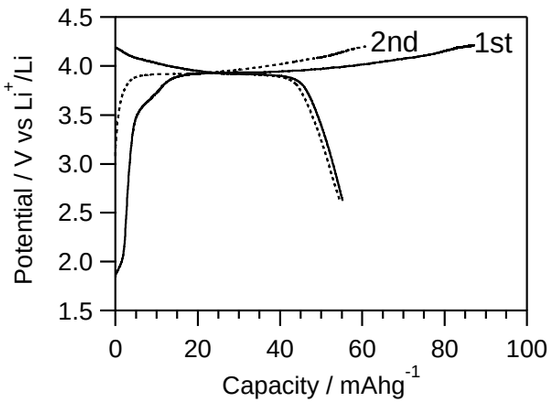

Figure 2 Charge-discharge curves of the epitaxial $LiCoO_2$ (104) film on the Nb 0.5wt%: $SrTiO_3$ (100) substrate.

[1] N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, Nat. Mater. **10** (2011) 682.
[2] T. Ohnishi, B. T. Hang, X. Xu, M. Osada, K. Takada, J. Mater. Res. **25** (2010) 1886.
[3] T. Ohnishi, T. Takada, Appl. Phys. Express **5** (2012) 055502.
[4] X. X. Xu, K. Takada, K. Fukuda, T. Ohnishi, K. Akatsuka, M. Osada, B. T. Hang, K. Kumagai, T. Sekiguchi, T. Sasaki, Energy Environ. Sci. **4** (2011) 3509.