Local crystalline structures of LiCoO₂ nanofilm cathodes in a lithium ion battery have been spectroscopically elucidated through confocal Raman imaging analysis at high spatial resolution of several hundred nanometers. A significant difference in the crystalline structure is found between the nanometric thin films and bulk powders. Thermally induced local decomposition of LiCoO₂ into an impurity phase on the films has also been revealed along with the mechanism of the temperature-triggered decomposition process. Moreover, frequency-based Raman imaging enables us to locally probe spatial separation between stoichiometric (LiCoO₂) and non-stoichiometric (Li₁₋ₓCoO₂, 0 < x < 1) crystal phases on the thin films. Such local crystalline analysis is a promising approach to provide new insights into the degradation mechanism of lithium-ion batteries, which would result in improving the performance of thin-film-based lithium-ion batteries.

**Keywords** Li-ion battery, Raman spectroscopy, lithium cobalt oxide, crystalline structure

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Experimental

LiCoO$_2$ thin films were prepared by sol-gel and spin-coating techniques. Li acetate (2.2 mM) and Co acetate (2.0 mM) were dissolved into ethanol with a Li/Co molar ratio of 1.1:1. Citric acid (2.0 mM) was used as a chelating agent, and was added to the solution. In order to form a sol colloid, the solution was stirred for 4 days until it turned translucent and brownish-red in color. The resultant sol was spin-coated onto silicon substrates at a rotational speed of 3000 rpm for 30 s. The sol films were pre-heated at 100°C for 5 min, and subsequently dried until a gel was formed. The gel films were heated again at a ramp rate of 40°C/min in air with the use of a furnace, and then calcined for 60 min at different temperatures in the range of 400 - 900°C. The sol-gel and subsequent spin-coating processes resulted in thin films with thickness of 150 - 200 nm which was confirmed by cross-sectional topographical measurements using atomic force microscopy.

Raman spectral imaging was performed using a line-scan confocal Raman microscope (Raman 11, Nanophoton Corp.) with an excitation wavelength of 532 nm. The microscope excited and detected Raman scattering simultaneously from 400 points on a sample illuminated by a focused line beam, enabling us to perform imaging several hundred times faster than conventional point-scan imaging. The spatial resolution of the microscope was ~350 nm with a 0.9 NA objective lens. The laser power density was set to ~0.1 W/cm$^2$ during Raman spectral imaging in order to avoid laser-induced phase transition of the LiCoO$_2$ crystalline structure.

Results and Discussion

Crystalline structures of the fabricated LiCoO$_2$ thin films were characterized by Raman spectroscopy. Figure 1(a) shows typically-observed Raman spectra of thin films fabricated by the sol-gel process at calcination temperatures ranging from 400 to 900°C. There are only two distinct peaks observed in the spectra of the thin films calcined at 400 - 700°C. The lower-frequency mode at 487 cm$^{-1}$ corresponds to the O-Co-O bending (E$_{g}$) mode, while the higher-frequency mode at 596 cm$^{-1}$ corresponds to the O-Co-O stretching (A$_{1g}$) mode. The two Raman bands at 487 and 596 cm$^{-1}$ are the main fingerprints of the layered rock-salt crystalline structure of LiCoO$_2$ with a rhombohedral lattice (space group R3m).

However, at a calcination temperature of 800°C, an additional new peak is observed at 693 cm$^{-1}$, and assigned to a characteristic vibrational mode of the spinel type Co$_3$O$_4$.$^{11}$ As the calcination temperature further increases up to 900°C, the Raman intensity of Co$_3$O$_4$ at 693 cm$^{-1}$ increases while the Raman intensity of the layered rock-salt LiCoO$_2$ at 596 cm$^{-1}$ vanishes. This result shows that lithium ions were completely extracted from LiCoO$_2$ at 900°C.

For a comparison, bulk powders of LiCoO$_2$ were also prepared by the sol-gel method under exactly the same conditions as for the synthesis of thin films, but deposited onto silicon substrates without the spin-coating process. Raman spectra of the powders calcined at temperatures of 400 - 900°C are shown in Fig. 1(b). Unlike the thin films, the powder calcined at 400°C possesses the distinct four Raman bands. The Raman-active peaks observed at 451, 488, 587 and 606 cm$^{-1}$ are assigned to F$_{2g}$, E$_{g}$, A$_{1g}$, and F$_{2g}$ modes, respectively. These are known as characteristic Raman modes of the crystalline structure of LiCoO$_2$ with a cubic lattice (space group Fd$ar{3}$m).$^{11}$ The lowest-frequency peak at 451 cm$^{-1}$ is isolated from the peaks of the layered rock-salt R$ar{3}$m LiCoO$_2$ phase, whereas the other peaks of the Fd$ar{3}$m LiCoO$_2$ phase are overlapped with, or close to, the peaks of the layered rock-salt LiCoO$_2$. In order to support the results, we performed XRD measurements to characterize LiCoO$_2$ powders calcined at 400 and 500°C were single phase of Fd$ar{3}$m LiCoO$_2$ (Fig. S1, Supporting Information). The Raman intensity of the lowest-frequency peak gradually decreases as the calcination temperature increased to 700°C. On the other hand, the E$_{g}$ mode of the layered rock-salt R$ar{3}$m LiCoO$_2$ phase appears at 596 cm$^{-1}$, and becomes pronounced due to the suppression of the neighboring A$_{1g}$, and F$_{2g}$ modes of the Fd$ar{3}$m LiCoO$_2$ phase. The powder calcined at 800°C exhibits the vibrational mode of Co$_3$O$_4$ at 693 cm$^{-1}$ along with the modes of the layered rock-salt R$ar{3}$m LiCoO$_2$ phase. The intensity of Co$_3$O$_4$ increases with increasing the calcination temperature up to 900°C. Calcination-temperature-dependent spectral changes of LiCoO$_2$ powders (but not thin films) have been studied so far by some research groups,$^{14–16}$ which show similar results to ours where low calcination temperatures (400 - 500°C) prefer to synthesize the Fd$ar{3}$m LiCoO$_2$ phase, whereas high calcination temperatures (700 - 800°C) prefer to synthesize the layered rock-salt R$ar{3}$m LiCoO$_2$ phase.

Spectroscopically identified compounds of both thin films and powders calcined at different temperatures are summarized in Table 1 together with their crystalline structures. A crucial difference of crystalline structures between thin films and
powders is found in the case of low calcination temperatures (400 and 500°C). At low calcination temperatures, the thin films possess the layered R\textsuperscript{3m} phase while the powders are composed of the Fd\textsuperscript{3m} phase. One of the possible causes for the different crystalline structures is the difference in the inner temperature between the film and the powder, even under the same calcination temperature. In order to investigate the inner temperature effect, we estimated the time-dependent temperature distribution inside the film and the powder under a constant outer heating temperature (i.e. setting temperature of the furnace) of 400°C applied for 60 min. The time-dependent inner temperature is calculated by solving the simple transient heat-conduction equation with Laplace transform technique\textsuperscript{17} using the initial conditions (outer temperature, film thickness (T), powder diameter (D), and thermal diffusivity of the film). It is found that although the temperature at the innermost part of the powder (D: 5 μm) reaches the outer temperature much more slowly than that of the film (T: 200 nm), the innermost temperatures of both the thin film and the powder reach close to the outer calcination temperature within 2 min. The calculation result indicates that both the film and the powder are entirely and homogeneously heated under the set heating temperature (400°C) during calcination for 60 min, i.e. there is no significant difference in temperature distribution between the film and the powder during calcination. Hence, the temperature is not the main cause for the difference in the crystal structures between the film and the powder. Another possible cause is the difference in the amount of reactive oxygen surrounding the film and the powder during calcination. When the sol is deposited onto the silicon substrate and heated, atmospheric oxygen existing at the interface between the sol and the substrate tends to be transported across the native oxide (SiO\textsubscript{2}) towards the silicon surface for thermal oxidization, resulting in a reduction of the partial oxygen pressure in the vicinity of the sol-substrate interface. Considering that the interfacial surface-to-volume ratio of the film (T: 200 nm) is at least 25 times larger than that of the powder (D: 5 μm), a larger portion of the thin film is exposed to low atmospheric oxygen at the interface than the powder. Since lower partial pressure of oxygen is known to preferentially form the layered rock-salt crystalline structure,\textsuperscript{18} the thin film is more likely to form the layered rock-salt than the powder, even at low temperature.

It is also found that smaller grain size (volume) in the layered rock-salt thin films is obtained with a lower calcination temperature (Fig. S1, Supporting Information). The small grain size obtained using the low temperature leads to a large reactive surface area during battery operation, which would improve the cell performance. On the contrary, as shown in Table 1, the layered LiCoO\textsubscript{2} powders were fabricated only at high calcination temperatures, which was associated with large grain size in the powder. Thus, thin films would be better than powders in terms of the high electrochemical reactivity as a cathode.

It should also be noted that lithium silicate is likely to be generated at the interface between LiCoO\textsubscript{2} and Si at elevated temperatures, which would induce lithium de-intercalation from LiCoO\textsubscript{2} to Si. The side reaction would promote/accelerate the decomposition of LiCoO\textsubscript{2} to Co\textsubscript{3}O\textsubscript{4} by lithium extraction with increasing the calcination temperature. However, the lithium silicate is too thin to be probed by our Raman measurement.

Raman imaging of the thin films was performed to analyze local distribution of the synthesized compounds in the thin films. Figures 2(a) to 2(c) show the Raman images of the thin films calcined at 400, 600 and 800°C, respectively. The images are constructed by merging Raman intensity images at 596 and 693 cm\textsuperscript{-1}, which are displayed in red and green, respectively. Red-colored maps represent the spatial distribution of the layered rock-salt LiCoO\textsubscript{2} while the green-colored maps represent that of the spinel Co\textsubscript{3}O\textsubscript{4}. In Fig. 2(a), only the red-color is entirely observed, confirming that the layered rock-salt LiCoO\textsubscript{2} is present in the thin film without Co\textsubscript{3}O\textsubscript{4} and distributed all over the imaging area on the silicon substrate. In Fig. 2(b), however, a partially green-colored region is observed along with an entirely red-colored region, which reveals that the layered LiCoO\textsubscript{2} is locally decomposed and transformed into an impurity domain of Co\textsubscript{3}O\textsubscript{4} at the calcination temperature of 600°C. The locally-decomposed area is ~480 nm\textsuperscript{2} which is estimated from the averaged lateral size of the green-colored Raman intensity spots. However, at a high calcination temperature of 800°C,
both the density and the size of the impurity domain are remarkably increased, as shown in Fig. 2(c). Figure 2(c) also tells us that LiCoO$_2$ and Co$_3$O$_4$ phases coexist only at the boundary surface of the Co$_3$O$_4$ impurity domain, which is seen in yellow (i.e. mixed color of red and green) surrounding the green spots. This result indicates that at the elevated temperature, the decomposition of LiCoO$_2$ into Co$_3$O$_4$ was evolved from the inner to the outer part of the impurity Co$_3$O$_4$ domain along with the increase in size.

Figure 2(d) shows a bright-field reflection image of the same area of Fig. 2(c), providing information on the surface morphology of the thin film. There is no significant correlation between the bright field and the Raman images in terms of image contrast. Thus, the local spatial distribution of LiCoO$_2$ and Co$_3$O$_4$ together with their crystal structures can be separately analyzed only from the Raman image and not from the morphological image. Even from SEM images with much higher spatial resolution than optical images, the local distribution of LiCoO$_2$ and Co$_3$O$_4$ is not distinguishable because there are no distinct differences in shape and size of grain structures in the thin film (Fig. S2(c), Supporting Information).

Figure 3(a) shows a Raman image that was measured in another area of the thin film calcined at 400°C. The image is constructed with the integrated intensity in the frequency region from 440 - 500 cm$^{-1}$, which includes the Raman band of the layered rock-salt LiCoO$_2$. The intensity-based image shows that the imaging area is fully and almost uniformly covered with the thin film of the layered rock-salt LiCoO$_2$, which is similarly seen in the image of Fig. 2(a). Figure 3(b) shows the Raman spectra measured at the positions (i) - (iii) in Fig. 3(a). Significant changes in the Raman spectral shape are observed depending on the measurement position. At position (i), a typical single Raman peak is observed at 488 cm$^{-1}$ originating from the $E_g$ mode of the layered LiCoO$_2$. At the positions (ii) and (iii), the Raman peak seems to be broadened owing to the presence of an additional peak at the lower frequency which is indicated by the blue arrow in the spectra. The higher frequency peak, indicated by the red arrow in the spectra, is slightly down-shifted at these positions, and the intensity of the peak decreases. These characteristic spectral changes observed at positions (ii) and (iii) are known to be caused by an expansion of the c-axis length as lithium ions are deinserted, indicating non-stoichiometric lithium cobalt oxides (Li$_{1-x}$CoO$_2$). The presence of the lower frequency peak is explained by the existence of an additional rhombohedral crystal structure with different size from the original rhombohedral structure to which the higher frequency peak is attributed.

Figure 3(c) shows a histogram of the peak frequency extracted from all of the spectra measured in the imaging area. Red- and blue-colored bars depict frequency distributions of the higher and lower frequency components, respectively. The histogram of the lower-frequency component is fitted with a single Gaussian curve, whereas the histogram of the higher-frequency component is fitted with triple Gaussian curves, which are marked as A, B and C. Phase A of the higher-frequency component is observed in association with the lower-frequency component, indicating the coexistence of two types of rhombohedral structures with different size. According to XRD and Raman studies, the coexistence is observed for non-stoichiometric Li$_{1-x}$CoO$_2$ with $0.25 < x < 0.47$. By contrast, phases B and C of the higher frequency component appear without the lower-frequency component, exhibiting a single peak in Raman spectra. Based on previous XRD and Raman studies, phase C is attributed to stoichiometric LiCoO$_2$ (i.e. $x = 0$) because of almost no frequency shift from the original frequency of 488 cm$^{-1}$. Phase B, on the other hand, exhibits slightly down-shifted frequencies from the original frequency by $-4$ cm$^{-1}$, indicating the non-stoichiometric phase with $0 < x < 0.2$.

In order to investigate the spatial distribution of three different phases (A, B and C) in the imaging area, a Raman image is constructed with the frequencies of the higher frequency component, which is shown in Fig. 3(d). Frequencies of phase A are dominant on the left middle and bottom region of the image while those of phase C on the right middle and top region. Phase B is found to be located along the boundary between phases A and C. This result indicates that the position-dependent phase separation between the stoichiometric phase ($x = 0$) and
the non-stoichiometric phase (0.25 < x < 0.47) occurs through the non-stoichiometric phase (0 < x < 0.25). Figure 3(e) shows another frequency-based Raman image constructed with the frequencies of the lower frequency component. The frequencies are distributed only in the same region where the frequencies of phase A in the higher frequency component are observed, which shows the coexistence of two rhombohedral crystal structures with different size. In this region, however, the image contrasts of the lower and higher frequency components are slightly different. Since the value of the frequency is directly correlated with the degree of expansion of the rhombohedral crystal lattice in the c-axis,19 the difference in the image contrast indicates that the level of crystal expansion in the c-axis for each rhombohedral structure is locally different.

Although a non-stoichiometric phase is typically produced by post-fabrication procedures, such as chemical20 and electrochemical21 delithiations, our as-prepared thin film contained the non-stoichiometric phase without any delithiation procedures. The non-stoichiometric phase of our thin film was distributed in only a small part of the thin film, while the stoichiometric phase comprised a large part of the film. This is because spatial temperature gradient of the calcination induced local lithium evaporations, resulting in a small amount of the lithium-deficient non-stoichiometric phase (Li1–xCoO2) along with a large amount of the stoichiometric phase (LiCoO2).

Finally, laser-induced changes of LiCoO2 crystalline structures were investigated on the thin film synthesized at a calcination temperature of 400°C. The incident laser light in the line shape with an excitation wavelength of 532 nm was focused onto the thin film with a different laser power density ranging from 0.5 to 5 mW/μm2. After each laser irradiation, Raman spectrum was measured using the same laser light, but with a reduced power density of 0.1 mW/μm2. As shown in Fig. 4(a), only two Raman bands of the layered LiCoO2 are observed in the case of laser irradiation under a low power density of 0.5 mW/μm2. However, since the irradiation power density was set to 1.5 mW/μm2, a weak, but clear, Raman peak of the spinel Co3O4 appears at 693 cm⁻¹, while the Raman peak intensity of LiCoO2 slightly decreases. By increasing the irradiation power density to 3.5 mW/μm², a gradual increase in the peak intensity of Co3O4 is observed along with further decrease in the intensity of the layered LiCoO2 at 596 cm⁻¹. Considering that LiCoO2 has strong absorption at the wavelength of the irradiation light due to the Co-3d transition band,15 laser-induced heating effect is enhanced under the increased laser power density, which promotes thermally induced decomposition of LiCoO2 into Co3O4. However, when the irradiation power density is increased to 5 mW/μm², both the Raman intensities of LiCoO2 into Co3O4 slightly decreased. This result indicates that the thin film starts to be ablated under a high power density.

We also performed Raman imaging of the thin film with a low laser power density of 0.1 mW/μm² after intense laser focusing onto the film with a power density of 3.5 mW/μm². Figure 4(b) shows the Raman image constructed with the Raman intensities of LiCoO2 and Co3O4 in red and green colors, respectively. The spinel Co3O4 is dominantly seen inside the intensely irradiated region surrounded by the yellow dotted line in Fig. 4(b). In contrast, the strongest Raman intensity of LiCoO2 is observed at the slightly outer sides of the intensely irradiated region although such a strong Raman intensity was not observed before the intense irradiation. For a more detailed analysis of the position-dependent Raman intensity, the Raman intensity profiles of both LiCoO2 and Co3O4 along the dotted white line in Fig. 4(b) are shown in Fig. 4(c). The Raman intensity of Co3O4 is maximized...
at the center of the intensely-focused region because of the strongest decomposition irradiating intensity in the center, resulting in the largest decomposition yield of LiCoO$_2$ into Co$_3$O$_4$ under the highest laser-induced temperature. The intensity gradually decreases while moving away from the center, but still remains even outside of the intensely-irradiated region. This result indicates that the laser-induced thermal energy laterally diffuses in the thin film, and is still large enough to induce the decomposition even out of the irradiated area. Thus, the intensity profile of Co$_3$O$_4$ reflects the laser-induced temperature profile over the thin film. Furthermore, the Raman intensity of LiCoO$_2$ starts to increase at the lateral position from –2 to –1 μm in Fig. 4(c), indicating formation of higher crystalline structures of the layered LiCoO$_2$ due to thermally-assisted crystalline ordering with increasing the laser-induced temperature. However, at the lateral position from –1 to 0 μm, the intensity starts to decrease because LiCoO$_2$ starts to be decomposed into Co$_3$O$_4$.

Conclusions

In conclusion, wide-field confocal Raman imaging analysis has been performed to investigate local crystalline structures of LiCoO$_2$ thin-film cathodes fabricated by the sol-gel and spin-coating processes. It spectroscopically proves that the thin films consist entirely of the layered rock-salt R$3m$ LiCoO$_2$ phase under a low calcination temperature of the sol-gel process, while the bulk powders consist of the Fd$3m$ LiCoO$_2$ phase under low temperature. Moreover, thermally induced decomposition of the layered rock-salt LiCoO$_2$ into the spinel Co$_3$O$_4$ has been qualitatively analyzed along with quantitative measurement of size and density of the locally decomposed domains. The high-resolution Raman imaging technique also enabled us to observe the local existence of non-stoichiometric Li$_{1+2x}$CoO$_2$ ($0 < x < 1$) in a thin film calcined at a low temperature of 400°C. The local distribution of the non-stoichiometric phase was successfully visualized separately from the stoichiometric phase, which has never been observed by means of other analytical techniques. In forthcoming work, an in situ Raman imaging analysis will be performed. This approach will allow us to elucidate the effects of the local crystalline structures of the thin films on the electrochemical performance of lithium-ion batteries, which would provide new insights into the degradation mechanism of lithium-ion batteries.

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Supporting Information

XRD patterns of LiCoO$_2$ powders prepared at different temperatures (Fig. S1). SEM images of LiCoO$_2$ thin films calcinated at different temperature (Fig. S2). These materials are available free of charge on the Web at http://www.jsac.or.jp/analsci/.

References