Intrinsic Electrochemical Characteristics in the Individual Needle-like LiCoO₂ Crystals Synthesized by Flux Growth

Kei NISHIKAWA,a,* Nobuyuki ZETTSU,b,c Katsuya TESHIMA,b,c and Kiyoshi KANAMURA d,e

ABSTRACT
The intrinsic electrochemical characteristics of needle-like LiCoO₂ crystals with a hexagonal cylindrical shape were studied by the single particle measurement technique. The needle-like LiCoO₂ crystals were synthesized by the flux growth method. Single-particle Raman spectroscopy and galvanostatic charge-discharge tests at different electrical contact points in one needle-like LiCoO₂ crystal revealed that the crystal has homogeneous intercalation/deintercalation characteristics throughout the long axis. This suggests that the electron conductivity is high on a 100 µm scale along that axis and that lithium ions are efficiently transferred from the electrolyte to the layer structure of the crystal. The charge rate characteristics of the needle-like LiCoO₂ crystals were also evaluated and compared to those of powdered LiCoO₂. The polarization curve analysis indicates that the needle-like LiCoO₂ particles had almost same exchange current density, \( i_0 \), as powdered LiCoO₂, which has a much smaller volume. These excellent electrochemical characteristics are considered to be due to the orientation of the \{104\} crystal face on the crystal sides, which is the preferential face for lithium ion transfer, and the larger effective surface area of the particles.

Keywords: Needle-like LiCoO₂, Single Particle Measurement, Li-ion Battery, Exchange Current Density

1. Introduction
High-energy-density secondary batteries are expected to be used as energy storage devices in environmentally friendly, sustainable energy systems. Li-ion batteries (LIBs) have very high energy densities and are used in mobile phones and laptop computers. Recently, LIBs have attracted significant attention because they are beginning to be utilized in plug-in hybrid electric vehicles and electric vehicles. LiCoO₂ is the most popular positive electrode material for LIBs since the reversible lithium intercalation reaction is reported by Goodenough et al. LiCoO₂ has a layered crystal structure and crystallizes in space group \( R \overline{3} m \). Li⁺ ions can be reversibly extracted from and inserted into the Li planes in the Li₂CoO₂ layer structure. For Li₂CoO₂, until \( x > 0.5 \), the reversibility is excellent and sufficient for use as a battery electrode. Many investigations have been carried out to understand the charge and discharge mechanism and improve the electrochemical performance of LIBs. The LIB electrode is a “composite electrode,” composed of active materials, conductive agents, and binders. Therefore, although the electrochemical characteristics of these composite electrodes must be evaluated from the viewpoint of battery engineering, it is not easy to distinguish the intrinsic properties of the active materials from those of the other materials in the composite electrode. However, we have used the single particle measurement technique to investigate the intrinsic properties of the active materials.

In this technique, a microprobe is placed in contact with an active material particle at the micrometer scale. Dokko et al. reported that commercial LiCoO₂ particles have been evaluated by this technique and have excellent rate characteristics. Clémençon et al. used in-situ atomic force microscopy (AFM) to study a LiCoO₂ crystal and reveal the dimensional changes along the \( c \) axis. LIBs must have excellent (high) rate characteristics. In particular, many investigations have focused on decreasing the Li⁺ ion diffusion length in the particles of the active material. Therefore, nano-sized active materials have been designed to have high rate charge and discharge performance. However, reducing the size of the active materials to the nanoscale increases both the cost of synthesis and the surface area. Although a large surface area is advantageous for the apparent current density, it is disadvantageous because side reactions increase.

In this study, needle-like LiCoO₂ crystals were synthesized by the flux growth method and their properties were investigated. The flux growth method is a very simple technique that allows the preparation of idiomorphic crystals without any thermal strain or defects from the liquid phase; furthermore, this technique also allows control over the morphology and size of the target materials. LiCoO₂ crystal growth by the flux method has been reported by Akimoto et al. As mentioned, LiCoO₂ has a layered structure. Therefore, it is easy to imagine that one particular crystal plane is superior for Li⁺ ion transfer in the crystal lattice. Our previous investigations have shown that the needle-like LiCoO₂ were surrounded by the \{104\} plane, as determined by X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements. Furthermore, electrochemical measurements concerning cyclability and the discharge rate characteristics of LiCoO₂ have been reported. In this study, the structural and electrochemical
uniformity of the needle-like LiCoO$_2$ crystals was investigated, and, using the single particle measurement technique, we evaluated the electrochemical characteristics of the needle-like particles and compared them with those of a commercial powder of LiCoO$_2$ particles.

2. Experimental

The needle-like LiCoO$_2$ material was synthesized by the flux method. CoO whiskers and LiOH·H$_2$O were used as the starting materials. NaCl was used as the flux. A homogeneous mixture of the starting materials was placed in a Pt crucible, heated to 1173 K, and maintained at this temperature for 5 h. The cooling of the sample was highly controlled, and details of this procedure have been described previously. The characterization of the LiCoO$_2$ was conducted by micro-Raman spectroscopy (LabRam, Horiba-Jobin Yvon). For the single particle measurements, a lab-made Pt microprobe was used to make electrical connection with a needle-like LiCoO$_2$ particle; details of the fabrication procedure have been described elsewhere. Before the measurement, the Pt microprobe was subjected to cyclic voltammetry in an aqueous 0.5 M H$_2$SO$_4$ solution for the cleaning. The single particle measurements were carried out in a super-dry room at room temperature (298 K). The dew point of the room was maintained below 223 K. The electrochemical cell was a two-electrode system with a Li metal counter electrode. The electrolyte was a mixed solvent of propylene carbonate and ethylene carbonate (1:1 by volume) containing 1 mol dm$^{-3}$ LiPF$_6$ (Kishida Chemical Co., Ltd.). Constant current charge and discharge measurements were conducted by using an electrochemical analyzer (SP-150, BioLogic) with a low-current probe. The potential range of the measurement was 3.0–4.2 V vs. the Li metal counter electrode.

3. Results and Discussion

The morphology of the LiCoO$_2$ crystals reflects that of the CoO whiskers that were used as the starting material in the flux growth synthesis, and field emission scanning electron microscopy (FE-SEM) images of LiCoO$_2$ crystals have been reported previously. The synthesized LiCoO$_2$ particles had a needle-like shape with a uniform diameter of several micrometers. The hexagonal cylindrical shape reflects the crystal structure of LiCoO$_2$. Previously, XRD and TEM analysis have revealed that the side face of the crystals is the {104} plane, and this morphology is expected to be preferable for Li insertion and extraction because the LiCoO$_2$ has a layered rock salt structure. The uniformity of the LiCoO$_2$ crystals in the direction of the long axis was evaluated by micro-Raman spectroscopy. The Raman spectra were measured at three different points of one needle-like LiCoO$_2$ particle, as shown in Fig. 1. The green line in Fig. 1 represents the Raman spectroscopy results of a commercial LiCoO$_2$ powder. Both peaks for the Eg and A$_{1g}$ modes of the needle-like LiCoO$_2$ are large. According to Inaba et al., the Eg and A$_{1g}$ modes correspond to peaks at 486 and 596 cm$^{-1}$, respectively. Therefore, the micro-Raman results for the needle-like LiCoO$_2$ agree well with those of Inaba. The reason for the peak shift of commercial LiCoO$_2$ powder is not discussed in detail here; however, the peaks may be shifted due to the poor crystallinity of the commercial powdered LiCoO$_2$ compared to that of the needle-like LiCoO$_2$ particles. Furthermore, a very small peak at 680 cm$^{-1}$, which corresponds to the cubic Co$_2$O$_3$ phase, was detected as an impurity, indicating that the needle-like LiCoO$_2$ crystals contain some impurities. However, XRD measurements carried out previously were unable to detect Co$_2$O$_3$ impurity phases, indicating that the impurity content is very low.

The single particle measurement technique was utilized to evaluate the electrochemical characteristics of the needle-like LiCoO$_2$ crystals. The contact resistance between the Pt microprobe and the LiCoO$_2$ crystal was negligible because the electrical conductivity of the LiCoO$_2$ material was almost $10^{-3}$ S cm$^{-1}$. Dokko et al. reported that contact resistance does not affect the electrochemical characteristics of LiCoO$_2$ particles. To examine the electrochemical uniformity of the particles, the dependence of the discharge rate characteristics of the contact point between the Pt microprobe and a needle-like LiCoO$_2$ crystal was determined. The Pt microprobe was placed in contact with the center and both side edges of the LiCoO$_2$ particle, as shown in Fig. 2(a). The microscope image shows the three different contact points as (i), (ii), and (iii). Figures 2(b), (c), and (d) show the discharge curves of the needle-like LiCoO$_2$ in contact with the microprobe at the center (i) and the sides of the particles (ii) and (iii), respectively. The applied discharge currents were 2, 20, and 200 nA. In these measurements, the Li$_{148}$Co$_{17}$O$_{2}$ (140 mAh g$^{-1}$) state was assumed to be the fully charged state. The theoretical capacity was estimated from the size of the LiCoO$_2$ crystals, as determined from the optical microscope images. In this estimation, the density of LiCoO$_2$ (5.05 g cm$^{-3}$) was used. The applied currents correspond to 2.7 C, 27 C, and 270 C for LiCoO$_2$. The charging current was fixed at 2 nA. Results from this analysis indicate that the discharging rate characteristic is independent of the contact point between the microprobe and the LiCoO$_2$ particle. Therefore, the needle-like LiCoO$_2$ crystal had excellent uniformity in the direction of the long axis, in agreement with the results of Raman spectra measurements shown in Fig. 1. This result suggests that the electron conductivity of the LiCoO$_2$ crystal is sufficient for high-speed discharge reactions. However, it is difficult to discuss the Li$^+$ ion conductivity along the long axis because there was enough electrolyte surrounding the needle-like LiCoO$_2$ particle during the measurement. We have assumed that the Li$^+$ ion transfer occurs mainly in the direction of the short axis (radius) of the LiCoO$_2$ needles. To understand the Li$^+$ ion conduction in LiCoO$_2$ in the direction of the long axis, we have to design an experiment where only the tip of the needle-like LiCoO$_2$ crystal is immersed in the electrolyte, thus limiting the Li transfer in...
In this study, the charge-rate characteristics (Li extraction reaction) were investigated because previous reports have investigated only the cycling stability and discharge rate characteristics. From the viewpoint of LIB applications, rapid charging and discharging are crucial. Figure 3 shows a microscope image of a measured needle-like LiCoO₂ crystal in the single particle measurement system (a), the charging curves for different charging current (b), the dependence of charging capacity on the applied charging current for the needle-like LiCoO₂ crystal (c), and those for the powdered LiCoO₂ with different particle sizes (d). The Pt micro-probe was placed in contact with the center of the particle in this measurement. The discharging current was fixed at 2 nA. The theoretical capacity was estimated from the size of the needle-like LiCoO₂ crystal shown in Fig. 3(a). The theoretical capacity was calculated to be about 1.27 nAh. This theoretical capacity agreed with the measured capacity at a charging current of 2 nA, as shown in Fig. 3(b); therefore, the measured capacity can be regarded as the full capacity of the LiCoO₂ crystal. Consequently, the current corresponds to a 1.6 C-rate at 2 nA and a 123 C-rate at 150 nA. Each of charging rate tests was conducted with 2 cycles. The potential plateau at 3.92 V at a C rate of 1.6 increased to 4.02 V at a C rate of 123, and the small two plateaus at 4.07 and 4.17 V were not observed at C rates greater than 57 (shown as a purple line). The increasing overpotential with the applied charging current is discussed later. The charge capacity at a C rate of 123 was maintained at over 90% compared with that at 1.6 C-rate, suggesting that the diffusion of Li⁺ ions in the solid state was not the rate-determining step, even at a C rate of 123. Figure 3(c) shows the charging capacity retention of the needle-like LiCoO₂ particles, while Fig. 3(d) shows those of powdered LiCoO₂ particles of different sizes. The diameters of the small powdered LiCoO₂ particles were about 10 µm, while those of other particles were about 14 µm. Therefore, the theoretical capacities of these LiCoO₂ particles were estimated to be 0.37 and 1.02 nAh, respectively. The measured capacities at low currents agree well with the estimated capacities. However, the trend in the charging capacity retention is different. The capacity of the larger particle decreased gradually with increasing applied charging current, falling drastically at C rates greater than 100. In contrast, the capacity of the smaller particle was almost constant, only decreasing as the C rate increased beyond 100. For the powdered LiCoO₂, the charge-rate characteristics were dependent on the particle size because, as the particle size increases, both the Li diffusion length and the number of grain boundaries in the particles increase. A detailed investigation concerning the size dependence of the positive electrode active materials is in progress. In contrast, the capacities of the needle-like LiCoO₂ particle showed a similar trend to that of the small particles of the powdered LiCoO₂ material. At a C rate of 100, the charging capacity of the needle-like particles was about 1.12 nAh (93% of the full capacity). For the large and small particles of powdered LiCoO₂, the capacities at 100 C were 0.68 nAh (72% full capacity) and 0.3 nAh (94% full capacity), respectively. Although the needle-like LiCoO₂ had a larger volume than the commercial LiCoO₂ powder, the high crystallinity of the material for Li insertion and extraction and the greater surface area resulted in the excellent charging rate performance, as well as the good discharging rate performance. To be more specific, the excellent rate performance may arise from the crystal orientation of the needle-like LiCoO₂ crystal surrounded by {104} planes, which are preferable for Li⁺-ion mass transfer. Furthermore, the larger effective surface area is also an important parameter. These results indicate that control of the crystal morphology is an effective way to achieve high rate performance and to utilize nano-sized primary particles. To analyze the intrinsic electrode kinetics for the charging reaction of the needle-like LiCoO₂ crystals, the electrode potential of the LiCoO₂ at a 20% state of charge (SOC) is plotted against the logarithm of the applied charging current density, i, in
Fig. 3(c). When the Li extraction rate is controlled by the charge transfer reaction, the Butler-Volmer equation describes the relationship between the applied current density and the overpotential.\textsuperscript{34} Figure 4 shows the quasi-polarization curve of the needle-like LiCoO\textsubscript{2} particles. For comparison, the results for the commercial powdered LiCoO\textsubscript{2} are also plotted in Fig. 4. The needle-like LiCoO\textsubscript{2} crystal performance is similar to that of the small powdered particles, even though the particle volumes are different; the capacity of the needle-like LiCoO\textsubscript{2} is 1.2 nAh, while that of the powder LiCoO\textsubscript{2} is 0.32 nAh. The current density was calculated from the apparent surface area of each LiCoO\textsubscript{2} particle. Here, we have assumed that the transfer coefficient ($\alpha$) for the anodic reaction is 0.5. The open-circuit voltage of Li\textsubscript{x}CoO\textsubscript{2} for $1 > x > 0.75$ is 3.92 V vs. Li\textsuperscript{+}/Li.\textsuperscript{4} A SOC of 20%, corresponding to Li\textsubscript{0.9}CoO\textsubscript{2}, was used for the quasi-polarization curve analysis. The exchange current density ($i_0$) for the needle-like LiCoO\textsubscript{2} crystal and the small particles of powdered LiCoO\textsubscript{2} was estimated to be 1.83 mA cm\textsuperscript{-2} by fitting a straight Tafel line and using the current density at the intercept at the equilibrium potential of 3.92 V vs. Li\textsuperscript{+}/Li. The Tafel line is represented by
\begin{equation}
\log i = \log i_0 + \frac{(1 - \alpha)F(E - \alpha\eta)}{2.303RT \eta}
\end{equation}
where $F$ is the Faraday constant, $R$ is the gas constant, $T$ is the temperature, and $\eta$ is the overpotential for the anodic reaction. In contrast, the large particles of powdered LiCoO\textsubscript{2} had larger overpotentials at the same current densities compared to those of the smaller and needle-like LiCoO\textsubscript{2} particles; this may be caused by the effect of more grain boundaries inside the particles and the longer Li\textsuperscript{+} ion diffusion length from the inside to the surface of the particles. As shown in the quasi-polarization curves in Fig. 4, the needle-like LiCoO\textsubscript{2} crystals have excellent electrochemical characteristics.

The uniform needle-like LiCoO\textsubscript{2} crystals have excellent electrochemical performance because of their favorable structure for Li\textsuperscript{+} ion transfer, formed by the flux growth method, which enables control over particle morphology. Such morphologically controlled materials can be used as model materials for discussing electronic and ionic conduction. Furthermore, the morphology control technique can be applied to other types of batteries, such as micro all-solid-state batteries,\textsuperscript{35} if the starting materials can be well-aligned with the substrates. Our results demonstrate that control over the morphology of the active material is a very efficient way to improve its intrinsic electrochemical characteristics. The investigation of the
dependence of the electrochemical characteristics of other positive materials on the particle morphology is one of our future research targets.

4. Conclusion

Needle-like LiCoO₂ crystals were synthesized by the flux method, and their electrochemical performance was evaluated by the single particle measurement technique. The uniformity of a needle-like LiCoO₂ crystal in the direction of the long axis was almost the same as that of the powdered LiCoO₂, although the electronic conductivity of LiCoO₂ is sufficient for operation at high rates of discharge. The charge rate characteristics were also excellent, in addition to the discharge rate characteristics reported previously. At charging rates greater than 100 C, the charging capacity remained higher than 90% because the crystal face orientation enabled the efficient transfer of Li⁺ ions from the layer structure to the particle surface. The polarization analysis for the charging reaction based on the quasi-Tafel equation indicates that the exchange current density, i₀, of the needle-like LiCoO₂ crystals was almost the same as that of the powdered LiCoO₂, although the volume of the needle-like LiCoO₂ particles was much larger. Thus, morphological control of the active material is an intelligent way to improve the intrinsic electrochemical performance, and the flux growth method is a powerful synthetic technique to achieve this control.

Acknowledgments

This work was supported by CREST, JST. Part of this research was financially supported by the TEPCO memorial foundation (12-003) and the Ministry of Education, Culture, Sports, Science and Technology (MEXT) Program for Development of Environmental Technology using Nanotechnology.

References