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Flux Growth of Hexagonal Cylindrical LiCoO₂ Crystals Surrounded by Li-ion Conducting Preferential Faces and Their Electrochemical Properties studied by Single-particle Measurements

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In this study, we demonstrated the template-mediated flux growth of one-dimensional LiCoO₂ single crystals surrounded by {104} faces in a hot solution of LiCl-KCl. The reaction and growth process were characterized by time-dependent X-ray diffraction and scanning electron microscopy. The transformation in the crystal shape from rectangular to hexagonal cylindrical was considered to be directly related to the gradual lithiation of the starting CoO whiskers. Single particle galvanostatic tests of the single-strand LiCoO₂ crystals were carried out. The LiCoO₂ crystals exhibited excellent rate performance; more than 65% of the full capacity was maintained under ca. 370 C. These characteristics likely resulted from the exposure of the {104} planes, since they were electrochemically active in layered LiCoO₂ with an α -NaFeO₂ structure and favored fast Li⁺ transportation. This finding will facilitate the development of new materials for advanced lithium ion rechargeable batteries.

Introduction

The shape-controlled synthesis of inorganic materials can influence many geometry-sensitive physical and chemical properties including luminescence, catalytic activity, surface energy, solubility, and conductivity of electrons and ions.^[1-7] As examples, quantum confinement of quantum dots, shape-dependent localized surface plasmon resonance in metal nanoparticles, and plane-sensitive catalytic activities have been developed by colloid chemists in the last decade. Advanced functional devices and catalysts such as quantum dot LEDs, lasers, solar cells, probes for biological diagnostic applications, Raman spectroscopy-enhancing materials, and activity-enhanced ORR catalysts have also been proposed.^[8-15] Very recently, researchers investigating secondary battery applications have confronted the urgent need to improve the specific power density of rechargeable batteries. Shape-controlled electrode active materials, including nanocrystals, nanoporous materials, and nanotubes have been investigated in the improvement of battery performance in terms of their enhanced charge-discharge rates, cycle stability, relatively flat charge-discharge plateau, thermal stability, and cation ordering.^[16-25] Most shape-controlled crystals are synthesized via low-temperature

processes such as polyol, sol-gel, hot-injection, and hydro- or solvothermal syntheses. However, as Zhou mentioned in the literature, high-temperature sintering processes are necessary to enhance crystallinity as well as to produce high-performance electrode active materials based on crystals such as LiCoO₂, LiMn₂O₄, LiFePO₄, and Li₄Ti₅O₁₂.^[26-29] However, such high-temperature sintering processes simultaneously lead to a large grain size and aggregation, which result in poor performance due to the increased lithium ion diffusion path, decreased contact with the electrolyte, and increased interfacial resistance. Thus, the synthesis of high-quality crystalline electrode materials with distinct shapes constitutes a major challenge in obtaining high-performance materials. As such, flux growth methods have recently garnered significant attention in the preparation of high-quality crystals for lithium ion battery applications. The flux growth method is the only way to obtain idiomorphic crystals without any thermal strain or defects from the liquid phase, and thus is quite advantageous as compared to other techniques.^[30] For instance, the flux growth of NaCl, NaCl-KCl, and LiCl-KCl enabled the growth of layered LiCoO₂, octahedral spinel LiMn₂O₄, and Li₄Ti₅O₁₂ crystals, which showed enhanced charge-discharge rates, cycle stability, and selective tolerance towards the loss of electrolyte-soluble transition metal ions in the crystals.^[31-34]

Among the many potential shapes, one-dimensional crystals are the most attractive because such ultra-long anisotropic crystals are expected to suppress aggregation and grain growth at high temperatures, possibly leading to decreased electronic resistance, as well as the formation of short circuits resulting from the penetration of active materials through the separator. However, the synthesis of one-dimensional single crystals with rhombohedral or cubic structures is difficult due to their crystallographic characteristics. Specifically, these crystals cannot naturally grow in a one-dimensional direction. Even though only a few papers regarding the hydrothermal synthesis of nanowires, nanorods, and

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branches composed of rhombohedral and cubic crystals have been reported, the relationship between the structure and electrochemical properties of crystals is not well understood because of the poor crystal quality (i.e., formation of polycrystals, agglomeration, and lack of uniform shape).^[20-22, 26] Here, we designed a strategic flux growth method to produce hexagonal cylindrical LiCoO₂ crystals, which were dominantly surrounded by {104} planes via the conversion of CoO whiskers as self-sacrificing templates in a chloride solution at high temperatures.

In this method, we used CoO whiskers grown from LiCl and Co powder in a LiCl-KCl mixed flux. Vapor grown carbon fibers (VGCFs) played a key role in the growth of the CoO whiskers. Curved imaging plate X-ray diffraction (IP-XRD) and TEM observations revealed that the CoO whiskers formed one-dimensional wires, with a flat rectangular cross-section which was dominantly covered with {110} planes and was grown along the <111> direction. The details regarding the synthetic procedures and crystallographic characterization of the CoO whiskers will be described elsewhere.

Results and discussion

To the best of our knowledge, this is the first report regarding the successful growth of one-dimensional LiCoO₂ single crystals using the flux growth method. Figure 1 displays the XRD profiles of the as-obtained product. All diffraction lines were in agreement with the ICDD data for LiCoO₂. Since the diffraction lines of CoO were not observed, single-phase LiCoO₂, which belongs to the *R-3m* space group, was formed. Notably, the relative intensities of the diffraction lines at $2\theta = 18.93/45.26$, assigned to 003_{LiCoO_2} and 104_{LiCoO_2} , were less than that of the ICDD data, suggesting that the LiCoO₂ crystals were dominantly covered with 104_{LiCoO_2} planes. The lattice parameters were determined as $a = 2.819$ and $c = 14.063$ Å.

Figure 2 shows the SEM images of the as-prepared LiCoO₂ crystals and CoO whiskers. The LiCoO₂ crystals resembled ultra-long wires, and maintained the one-dimensional structure of the CoO whiskers. Their average diameter and length was slightly larger at 2.5 μm and > 550 μm, respectively, possibly due to the penetration of Li ions into the cubic CoO lattice. Their magnified and cross-sectional profiles, as evaluated by SEM, illustrated the unique nature of the one-dimensional LiCoO₂ crystals. Specifically, individual LiCoO₂ crystals formed unusual structures in which numerous hexagonal plate-shaped crystals were stacked face-to-face one-dimensionally. Typically, LiCoO₂ crystals that form hexagonal platelet-shaped crystals are seen in liquid phase growth. It is well known that the hexagonal shape surrounded with a large *c*-plane is the result of a thermodynamically favored state produced under an oxidative atmosphere. Therefore, the transformation of the cross-section from

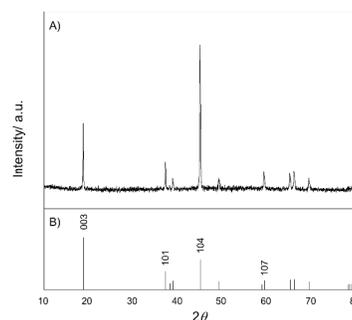


Figure 1. X-ray diffraction (XRD) profiles of (A) as-obtained product and (B) ICDD data for LiCoO₂ (PDF 75-0532).

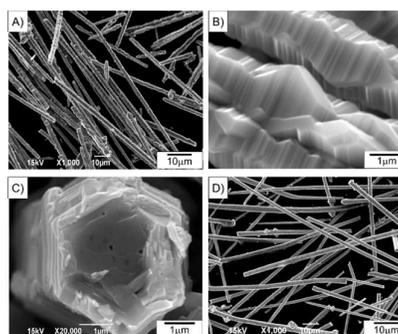


Figure 2. SEM images of (A-C) LiCoO₂ crystals with different magnifications, and (D) of the CoO whiskers.

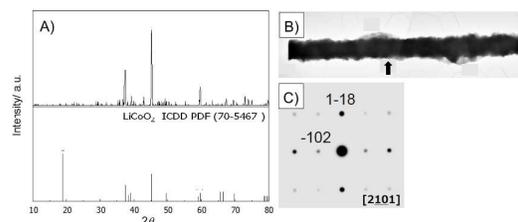


Figure 3. (A) Imaging plate-XRD of the one-dimensional LiCoO₂ crystals and the ICDD data for LiCoO₂ (PDF 75-0532). (B) TEM image of the one-dimensional LiCoO₂ crystals and (C,D) corresponding SAED patterns.

the flat rectangular shape of the CoO whiskers into the hexagonal shape of LiCoO₂ crystals in the molten LiCl-KCl mixed salt was reasonable and reflected the changes in the crystal structure from the cubic system of CoO to the rhombohedral system of LiCoO₂.

We performed imaging plate XRD (IP-XRD) measurements in order to elucidate the crystallographic nature of the single-strand LiCoO₂ crystals. The X-ray beam was incident to the surface of the one-dimensional LiCoO₂ crystal, perpendicular to its longitudinal direction. As shown in Figure 3A, three strong diffraction lines from the 101_{LiCoO_2} , 104_{LiCoO_2} , and 107_{LiCoO_2} planes were observed under the limited diffraction conditions. Owing to the disappearance of the diffraction line corresponding to the 003_{LiCoO_2} plane in the IP-XRD profile compared to that of the powder XRD shown in Figure 1, the longitudinal direction of the LiCoO₂ crystals was assigned to the <001> direction. Selected area electron diffraction (SAED) patterns coupled with TEM images were obtained for several regions of the one-dimensional LiCoO₂ crystals to further elucidate the

crystallographic nature. We adjusted the electron beam to graze the crystal surface. Figure 3C represents the SAED patterns obtained from the single LiCoO_2 crystal, indicated by the arrow in Figure 3B. Periodically ordered diffraction spots were observed without any additional spots or diffuse streaks, indicating that the one-dimensional LiCoO_2 crystal had high crystallinity. The diffraction spots were indexed as belonging to the $[2101]$ zone axis of single crystal LiCoO_2 , which confirmed that the LiCoO_2 crystal was a single crystal and the surface was covered with $\{102\}$ and $\{1-18\}$ planes.

To gain insight into the conversion mechanism responsible for this unusual morphology, we performed *in-situ* XRD measurements and carried out time-dependent *ex-situ* SEM observations. The samples were heated to designated temperatures, and were rapidly quenched with cool water prior to the SEM observations. As shown in Figure 4, the reaction was initiated at 800°C , which was similar to the melting point of NaCl flux. The diffraction lines were assigned to rocksalt-CoO, rocksalt- $\text{Li}_{0.14}\text{Co}_{0.86}\text{O}$, and minor rhombohedral LiCoO_2 . With an increased holding temperature of 900°C , the lithiation reaction progressed sequentially. Notably, the LiCoO_2 phase was the major product during the early stages of the reaction, even though the incompletely lithiated and unreacted CoO phase remained. This implied that the diffusion of Li^+ in the solid CoO whisker limited the reaction rate. Thus, the phase change from rocksalt to rhombohedral proceeded from the surface and the CoO phase remained at the core of the crystal. Figure 5 shows a schematic illustration of the cleavage plane of $(211)_{\text{CoO}}$ and $(2101)_{\text{LiCoO}_2}$. No significant changes in the arrangement of Co and O atoms occurred, even though the distance of the O-Co-O plane in CoO became slightly smaller and the symmetry of the unit cell was distorted due to the differences in the ionic radii of Co^{2+} in CoO and Co^{3+} in LiCoO_2 . This suggested that the CoO $\{110\}$ planes were favorable for the conversion to LiCoO_2 , as they maintained the original one-dimensional shape.

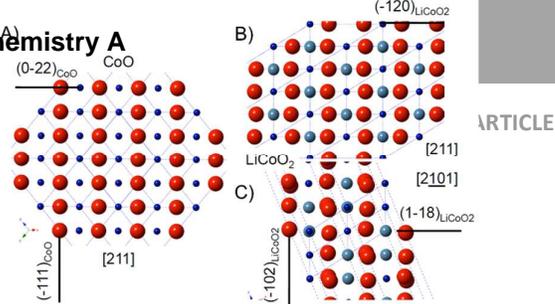


Figure 5. Schematic illustrations of (A) CoO (211) plane and (B, C) LiCoO_2 (211) and $(1-101)$.

Next, we carried out time-dependent SEM observations coupled with XRD measurements for further understanding the conversion mechanism and shape transformation. All samples were prepared individually prior to each SEM observation by quenching the reaction with cool water. There were many holes on the CoO whisker surface, which were not observed on the initial flat CoO whiskers (Figure 6A, B). These holes may have originated as a result of the formation of LiCoO_2 and rocksalt- $\text{Li}_{0.14}\text{Co}_{0.86}\text{O}$, which would lead to a reduction in volume and lattice distortion in the CoO crystals. The roughness of the surface increased with the increase of holding time. The lattice distortion and further Li^+ penetration promoted drastic morphology changes (Figure. 6C). A sharp zig-zag, step-like morphology was formed on the surface as lithiation proceeded. After the CoO crystals were fully lithiated, the LiCoO_2 formed an unusual structure in which numerous hexagonal plate-shaped crystals with sharp asymmetrical edges were stacked one-dimensionally (Figure. 6 D, E). CoO and LiCoO_2 exhibited low solubility in the LiCl-KCl flux, which we believe promoted the lithiation reaction while maintaining the original one-dimensional structure. The shape deformation possibly depended on the minimization of the surface-free energy of the LiCoO_2 crystals via the dissolution and precipitation reaction of minute amounts of LiCoO_2 , which were dissolved in the flux.

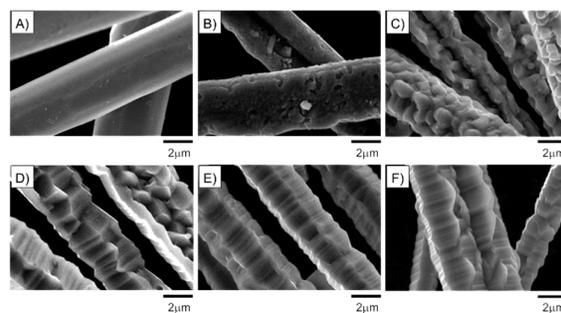


Figure 6. Time-dependent SEM images; (A) initial CoO whiskers, (B) 800°C , (C) 900°C , (D) 900°C for 1 h, (E) 900°C for 3 h, (F) 900°C for 5 h.

Single particle galvanostatic charge/discharge measurements were performed to study the intrinsic electrochemical properties of the one-dimensional LiCoO_2 crystals.^[35-38] A single LiCoO_2 crystal was contacted with a micro Pt electrode with a diameter of $20\ \mu\text{m}$ in an electrolyte composed of ethylene carbonate (EC) and propylene carbonate (PC) (1:1 v/v), containing 1 M of LiPF_6 . Figure. 7A shows the first 50 charge and discharge curves, measured at 3 nA for both charging and discharging in the potential range of 2.0-4.2 V vs. Li/Li^+ . The 3 nA corresponds to ca. 8.6 C rate, because the average specific capacity was estimated to be ca. 0.35 nA. One C rate indicates the current required to obtain a full charge in 1 h.

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Excellent reversibility with a high coulomb efficiency was observed after the second cycle even with a relatively large C rate, although some irreversible capacity was observed in the first cycle. This result implies that the ultra-long LiCoO₂ crystal was stable during 50 cycles of the rapid LiCoO₂ \rightleftharpoons Li_{0.50}CoO₂ + 0.5 Li⁺ + 0.5 e⁻ reaction. The average specific capacity was estimated to be ca. 0.35 nA h. Figure 7B shows the discharge curves measured at various currents ranging from 5 nA to 300 nA, corresponding to C rates of 1 to 429. The crystal was charged galvanostatically at 1 nA up to 4.2 V vs. Li/Li⁺ prior to all discharge measurements. Amazingly, the one-dimensional LiCoO₂ crystal maintained more than 65% of the full capacity at 300 nA discharge (only 8 s). These electrochemical responses are significantly better than those of commercially available LiCoO₂, as shown in Figure 7C. The LiCoO₂ polycrystal prepared via a solid-state reaction showed more than 50% loss of the full capacity at 300 nA, corresponding to 370 C. This result suggests that the crystal orientation of the LiCoO₂ crystal resulted in a better rate performance than that of the commercially available crystal. Because the electrode potential dropped as the current increased, there was a gradient in the concentration of Li in the single particle. Li⁺ diffusion in the solid phase is slower than that in a liquid electrolyte, suggesting that the rate performance should be influenced by the Li⁺ transfer process at the interface between active material crystals and liquid electrolytes, as well as the Li⁺ diffusion process from the surface to the center of the crystals. Figure 7D shows the capacity retention depending on the discharge current of both one-dimensional and commercially available irregular LiCoO₂. Assuming that the simple diffusion of Li⁺ ion occurs in the particle two-dimensionally from the surface to the center, the apparent diffusion coefficient of Li⁺ ion in the LiCoO₂ crystals can be estimated as follows: the diffusion length L is expressed as $L = (4Dt)^{1/2}$, where D is the apparent diffusion coefficient and t is time for diffusion.^[39, 40] L is the radius of the one-dimensional LiCoO₂ particle (2.8 μm). In case of 30 nA discharging, no discharge capacity loss was observed, and the time required for the discharge was 84 s. Therefore, this implies that a Li⁺ ion can diffuse from the surface to the center of the one-dimensional LiCoO₂ particle for 84 s. The apparent diffusion coefficient of Li⁺ in the particle is $2.3 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ based on those values. It is compatible with the apparent diffusion coefficient in other reports, which used the same technique for commercial LiCoO₂ particles.^[35]

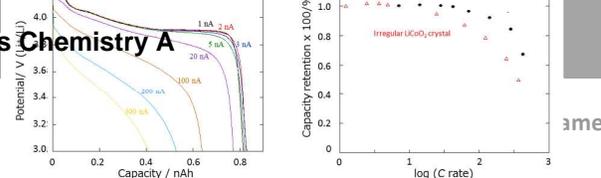


Figure 7. (A) First 50 charge and discharge curves of the one-dimensional LiCoO₂ single particle; (B) rate capabilities of the one-dimensional LiCoO₂ single crystal electrode and (C) that of the commercially available LiCoO₂ single particle electrode at 23°C; (D) the corresponding capacity retention characteristics under various rate conditions.

Experimental

Synthetic procedures. In a typical synthesis, 0.01 g of CoO whiskers and 0.01 g of LiOH·H₂O were gently mixed with 0.15 g of NaCl for 30 min using an agate mortar. The molar ratio of CoO and LiOH·H₂O was of 1:2. The Co concentration in the mixture was controlled to be 5 mol%. The homogeneous mixture was placed in a 30 cm³ Pt crucible. The loosely closed crucible was then placed in an electric furnace, heated to 900 °C at a rate of 900 °C·min⁻¹, and held at that temperature for 5 h. The crucible was cooled to 500 °C at a rate of 200 °C·h⁻¹. Finally, the crucible was naturally cooled to room temperature in the furnace. The crystals were separated from the remaining flux mixture using warm water. The morphology and average size of the grown LiCoO₂ crystals were characterized using field-emission-type scanning electron microscopy (FE-SEM, JEOL, JSM-7600F); the microscope was operated at an acceleration voltage of 15 kV. The phases and structures of the crystals were identified using X-ray diffraction analysis performed with Cu K α radiation ($\lambda = 0.15418 \text{ nm}$). The X-ray diffractometer (XRD, RIGAKU, SmartLab) and imaging plate XRD (IP-XRD, RIGAKU, RINT RAPID) were operated at 30 kV and 20 mA, with 2θ being in the range of 10–80°. The crystallographic characteristics of the LiCoO₂ crystal were characterized by using transmission electron microscopy (TEM, JEM-2010 EXII), and high-resolution transmission electron microscopy (HR-TEM, TOPCON, EM-002B) operated at 200 kV.

Single particle galvanostatic tests. A Pt micro-wire with 20 μm diameter was sealed in glass capillary.^[35] The tip of the glass-sealed Pt micro-wire was cut to yield a micro-disk, and then polished carefully to a mirror face. Cu was electrodeposited onto the Pt micro-disk tip at a constant current condition of 31.4 nA for 30 min in 0.6 M CuSO₄·5H₂O and 5×10^{-4} M H₂SO₄ aqueous solution, because of the prevention for the electrochemical reaction of Pt with Lit ion. The single particle measurement system was operated in the dry room. The micro electrode was manipulated by using a micromanipulator (QP-2RH, Microsupport) to contact the probe with a single-strand LiCoO₂ crystals under optical microscope (BX-51, Olympus) observation. The electrolyte composed of ethylene carbonate (EC) and propylene carbonate (PC) (1:1 v/v), containing 1 M of LiPF₆, from Kishida Chemical Co., Ltd.. The counter electrode was a Li foil supplied from Honjo Metal Co., Ltd. and the electrochemical measurements were performed with a two electrode system. The galvanostatic charging (lithiation) tests were carried out with an electrochemical analyser (ALS600D, BAS Inc.) up to 0.01 V vs. Li/Lit. The temperature was kept 295 K in the dry room.

Conclusions

We have shown experimentally the discovery of the previously unknown hexagonal cylindrical LiCoO₂ single crystal covered with {104} planes and its unusually high electrochemical performances. The one-dimensional LiCoO₂ crystal surrounded by large {104} planes can be prepared by template-mediated growth in a hot LiCl-KCl flux. The halides-flux growth approach with weak solvency power enabled to form the LiCoO₂ having an unusual structure in which numerous hexagonal plate-shaped crystals with sharp asymmetrical edges were stacked one-dimensionally. CoO and LiCoO₂ exhibited low solubility in the LiCl-KCl flux, which we believe promoted the lithiation reaction while maintaining the original one-dimensional structure. The shape deformation possibly depended on the minimization of the surface-free energy of the LiCoO₂ crystals via the dissolution and precipitation reaction of minute amounts of LiCoO₂, which were dissolved in the flux. Since the previously unknown hexagonal cylindrical LiCoO₂ single crystals showed unusually high electrochemical performances, shape-controlled synthesis of Li-ion conducting materials via flux growth may serve as a novel way to develop advanced lithium ion rechargeable batteries based on unusual shaped single crystal active materials.

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Flux Growth of Hexagonal Cylindrical LiCoO_2 Crystals Surrounded by Li-ion Conducting Preferential Faces and Their Electrochemical Properties studied by Single-particle Measurements

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Hexagonal cylindrical LiCoO_2 crystal surrounded by large $\{104\}$ planes prepared through template-mediated flux growth exhibits a fast Li^+ transfer and favorable electrochemical performance at high current rates.

