## Original Paper

# Growth of Large-diameter LiCoO$_2$ Single Crystals by the Traveling Solvent Floating Zone (TSFZ) Technique using a Tilting-Mirror-type Image Furnace

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For traveling solvent floating zone growth of large-diameter single crystals of LiCoO$_2$, the growth conditions, such as the slightly excess Li content in the feed, amount of solvent and the filament shape of the heating lamps, were optimized for various crystal diameters using a tilting-mirror-type image furnace. The stability of the molten zone was affected by the excess Li content in the feed and the amount of solvent. The optimum amount of solvent was linearly related to the square of the crystal diameter during growth. We successfully grew LiCoO$_2$ single crystals with a diameter of 13 mm and a length of 50 mm with a shiny visible character under the optimum growth conditions.

Key Words: *TSFZ Method, Lithium Cobalt Oxide, Cathode Material, All Solid State Batteries, Cylindrical Filament Type Lamp*

## 1. Introduction

Many researchers have recently focused on alternative energy sources to decrease global warming and environmental pollution [1]. Li-ion batteries (LIBs) are one of the most attractive energy storage technologies that were first introduced into the market by Sony in 1991 and have been widely accepted as power sources for portable electronics and mobile instruments, such as cellular phones, digital cameras and notebooks, because of their high energy and power density [2-7]. Layered lithium cobaltate LiCoO$_2$ has been commercially used as a cathode material in LIBs for over ten years, with extremely fast market growth [8]. This cathode material has excellent characteristics, such as high discharge potential, low molecular weight, high energy capacity, good charge/discharge performance, relative ease of synthesis and treatment, and stable and high discharge voltage, which is promising for commercial application of LIBs [9-17].

LiCoO$_2$ crystallizes into a layered rhombohedral structure where Li$^+$ ions move perpendicular to the $c$-axis [18,19]. The layered structure is the fundamental reason to expect high ionic conductivity in this type of structure. Due to the highly anisotropic ionic conductivity in LiCoO$_2$, LiCoO$_2$ single crystals with thicknesses perpendicular to the $c$-axis are strongly required as a cathode to enhance the capacity and charge/discharge rate of LIBs for the development of next generation all solid state LIBs [20,21].

Several authors have already reported the growth of LiCoO$_2$ single crystals with a diameter of 5 mm by floating zone (FZ) technique using high Li-excess feed up to 100 mol% excess Li$_2$CO$_3$ to compensate Li evaporation without solvent [22,23]. We have also grown high-quality single crystals of LiCoO$_2$ by the TSFZ technique with the feed of the stoichiometric LiCoO$_2$ and a solvent of 85 mol% Li$_2$O [21,24]. However, the diameter of the grown crystal was limited to 7 mm. The LiCoO$_2$ single crystals larger than a half inch diameter are required for the commercial application of cathodes to enhance the performance of LIBs. Up to date, there is no report on the TSFZ growth of LiCoO$_2$ single crystals of diameter more than half inch that is the main focus of this research. We had tried to grow LiCoO$_2$ single crystals with 10 mm in diameter by the TSFZ method using the feed of the stoichiometric LiCoO$_2$ and a solvent of 85 mol% Li$_2$O according to references 21 and 24. We found that the main problems on the periodical instability of the molten zone during

TSFZ growth of larger-diameter single crystals of LiCoO$_2$ were the higher Li evaporation and the contact between feed rod and the grown crystal. The higher lamp power was required for the crystal growth using the feeds of 10 mm in diameter compared to 7 mm in diameter. The higher lamp power enhanced not only evaporation of Li component from the molten zone but also deposition of cobalt oxide phase in the grown crystals. In addition, contact between the feed rod and the grown crystal occurred due to the deposition of cobalt oxide phase with a high melting temperature, which leads to instability in the molten zone during TSFZ growth. The stability of the molten zone surely affects the crystal quality. We expected that the filament shape of the heating lamps is effective on the heating efficiency for reduction of Li evaporation and the length of the molten zone for prevention of the contact. Solvent amount is also an important parameter to control the volume of molten zone during the TSFZ growth with increasing the crystal diameter. The periodic instability of the melting zone suggests that the Li concentration in the melting zone fluctuates periodically due to the alternating Li evaporation and cobalt oxide precipitation from the melting zone for TSFZ growth of the large-diameter crystals using the stoichiometric LiCoO$_2$ feeds. Therefore, addition of the excess Li$_2$CO$_3$ into the stoichiometric feed is necessary to compensate the excess amount of Li evaporation at a higher growth temperature for the growth of LiCoO$_2$ single crystals larger than 7 mm in diameter.

In this research article, we studied the effects of slightly excess Li content (2 mol% to 5 mol%) in the stoichiometric feed, the solvent amount and the filament shape of the heating lamps on the TSFZ growth of larger-diameter LiCoO$_2$ single crystals. In addition, we successfully grew large LiCoO$_2$ single crystals with a diameter of 13 mm with a metallic luster.

## 2. Experimental Procedure

Li$_2$CO$_3$ (Rare Metallic Co., Ltd. 99.9% purity) and Co$_3$O$_4$ (Rare Metallic Co., Ltd. 99.9% purity) powders were used as starting raw materials and mixed in a stoichiometric ratio. The mixed powders were calcined at 750 °C for 4 hours in an air atmosphere. The calcined LiCoO$_2$ powder and Li$_2$CO$_3$ powder were then mixed in 52 - 55 mol% Li$_2$O in the Co$_2$O$_3$-Li$_2$O phase diagram, placed into a rubber tube to form a cylindrical shape, and pressed under a cold isostatic pressure of 300 MPa to form a feed rod with a diameter of

10-15 mm and a length of 60 mm. The feed rod was sintered at 1050 °C for 8 hours in an oxygen atmosphere. Due to the incongruent melting behavior of LiCoO$_2$, a Li-excess solvent was used for the TSFZ growth. The calcined stoichiometric LiCoO$_2$ powder and Li$_2$CO$_3$ powder were mixed in 85 mol%Li$_2$O, formed into a cylindrical shape with a diameter of approximately 10-15 mm using a hydrostatic press, and then used as a solvent disk without sintering for TSFZ growth. The crystal growth was carried out by adopting a tilting-mirror-type image furnace (Crystal Systems Inc. model TLFZ-4000-H-VPO) with four ellipsoidal mirrors. All growth experiments were performed at a mirror tilt angle of $\theta = 10°$ due to the low convexity and high stability in this tilt condition [21]. The concept of the mirror tilt angle $\theta$ can be found in detail in our previous research article [21]. To study the effects of the filament shape of the heating lamps on the growth of large-diameter single crystals of LiCoO$_2$, halogen lamps with commercially available flat-type and prototype cylindrical-type filaments with a rated output of 300 W were used in the growth experiments, as shown in Fig.1. The filament size of the flat filament-type lamp was 7 mm square and 3 mm thick. In the case of the cylindrical filament-type lamp, the filament size was 9 mm in length with inner and outer lamp filament diameters of 4.5 mm and 5.5 mm, respectively.
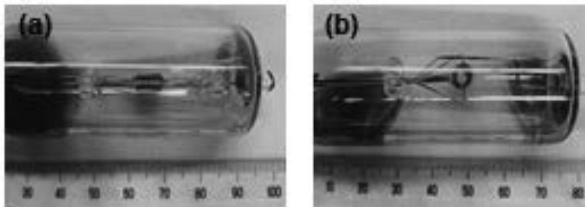


Fig.1　Photographs of 300 W (a) flat filament-type and (b) cylindrical filament-type lamps.

Before crystal growth experiments, a solvent disk was attached to the feed rod by melting. The procedure for the solvent attachment experiment has been described in our previous research article [21]. The direction of the seed crystal was [001] for the entire growth experiment. The growth conditions in all growth experiments were a growth rate of 5 mm/h, a growth atmosphere of Ar with a flow rate of 1.5 L/min and upper and lower shaft rotation rates of 12 rpm and 25 rpm, respectively, in opposite directions. The TSFZ growth was performed with various growth parameters, such as the excess Li content in the feed, the amount of solvent, the feed diameter and lamp filament type. To study the effects of excess Li content in the feed on the stability of the molten zone, excess Li content from the LiCoO$_2$ stoichiometric composition was varied from 2 mol% to 5 mol% during the growth of crystals with a diameter of 10 mm and 13 mm. The solvent amount is an important factor in obtaining a stable molten zone during TSFZ growth. It depends mainly on the feed diameter. To determine the optimum solvent amount for stable growth of large-diameter single crystals, the amount of solvent was also varied. The required lamp power for each growth experiment was estimated from the applied voltage and the voltage-lamp current proportionality of the halogen lamp. The effectiveness of the cylindrical-type filament of the heating lamp in the mirror-tilting furnace was confirmed by the long-term stability of the molten zone and crystal quality.

## 3. Results and Discussion

### 3.1 Effects of the filament shape of the heating lamps on the stability of the molten zone during TSFZ growth of large-diameter LiCoO$_2$ single crystals

The molten zone length is an important parameter to maintain a stable molten zone that depends not only on the growth conditions but also on the lamp heating conditions, such as the lamp filament

configuration and the focusing conditions from the heating lamp. Fig.2 shows photographs of two molten zones during the TSFZ growth of 10 mm diameter LiCoO$_2$ single crystals using tilting-mirror-type image furnaces with different filament types for the heating lamps. In the case of the flat filament-type lamp shown in Fig.1(a), the molten zone length was 6 mm and shorter as compared with the feed diameter due to the small heating region formed by the flat-type filament, as shown in Fig.2(a). As a result, periodic contact between the feed rod and the grown crystal occurred due to the insufficient gap between the feed rod and the grown crystals. In contrast, the molten zone length for the cylindrical filament-type lamp was increased to 8 mm, 2 mm longer than that for flat filament-type lamp, as shown in Fig.2(b). As a result, a highly stable molten zone, in which the gap between the feed rod and grown crystals was sufficient, was obtained during growth using cylindrical filament-type lamp.
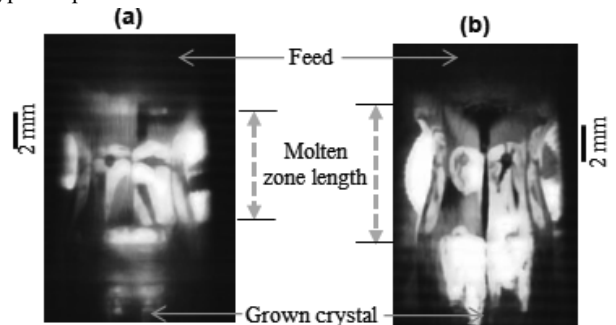


Fig.2　Photographs of molten zones during the growth of LiCoO$_2$ single crystals with a diameter of 10 mm using heating lamps of (a) flat-type and (b) cylindrical-type filament.

The heating region was significantly related to the filament size and shape. We realized that the focusing conditions for the heating lamp filament were strongly related to the stability of the molten zone during the growth experiment. Fig.3 shows a schematic focusing image for flat and cylindrical filament-type lamps at a mirror tilt angle of 10° for crystal diameter of 10 mm. For focusing using flat filament-type lamps of 3 mm thickness and 7 mm width,
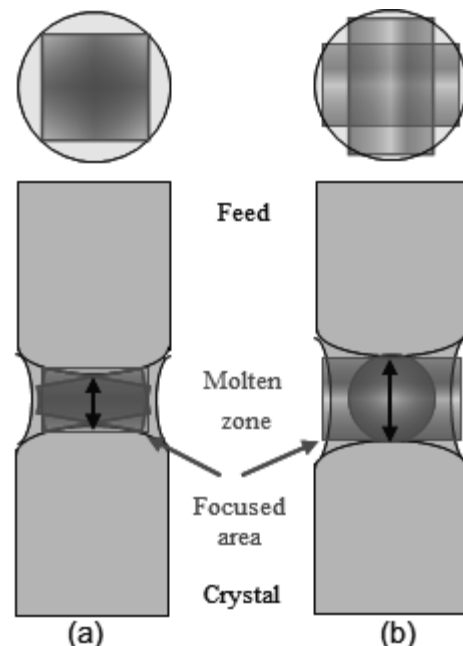


Fig.3　Schematic illustration of focusing images for flat (a) and cylindrical (b) type filament lamps at a mirror tilt angle of 10 ˚ for crystal diameter of 10 mm. The upper and lower drawings are the view from above and the side, respectively.

the high focusing region is narrow and short compared with the cylindrical filament-type lamps of 5.5 mm in outer diameter and 9 mm long. The focusing system of a narrow and short size is effective for growing small diameter crystals, but it causes contact between the feed rod and the crystal easily. In the cylindrical filament-type lamp, the focusing rays from the cylindrical-type filament were near the solid-liquid interface rather than at the center of the fusion zone since the temperature around the coiled filament was higher than that at the center, as shown in Fig.3(b). Therefore, the high focusing region is wide and long for cylindrical-type filament lamps. A stabilized molten zone avoiding the contact problem was achieved due to the high efficiency of the cylindrical-type filament.

## 3.2 Effects of the excess Li content of the feed and the amount of solvent on the TSFZ growth of large-diameter single crystals of LiCoO₂

The stability of the molten zone showed a strong relationship with the excess Li content of the feed and the amount of solvent during the TSFZ growth of large-diameter single crystals of $LiCoO_2$. As the feed diameter increased, the amount of Li evaporation from the melting zone also increased due to the highest required lamp power for crystal growth. The large amount of Li evaporation for growth using the feed rods of 10 mm caused the melting zone to become unstable periodically. To compensate for the excess Li evaporation from the molten zone during the TSFZ growth of large-diameter single crystals, the feed composition was changed to a excess Li content of 2 to 5 mol% $Li_2O$ from the $LiCoO_2$ stoichiometric composition, i.e. 52 to 55 mol% $Li_2CO_3$ in the $Co_2O_3 - Li_2O$ system. Figs. 4 and 5 show photographs of $LiCoO_2$ crystals with a diameter of 10 mm and 13 mm, respectively, grown with varying excess Li content in the feeds and amount of solvent by the tilting-mirror approach with cylindrical filament-type heating lamps.
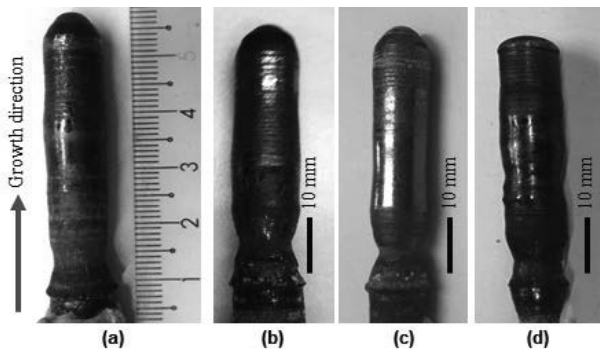


Fig.6  SEM images at (a) rough surface part and (b) luster surface part in the grown crystal.

To study the effects of the excess Li content in the feed on the TSFZ growth, only the excess Li content in the feed was varied while keeping the other growth parameters such as the solvent composition constant, as shown in Figs. 4(a to c) and 5(a to c). $LiCoO_2$ single crystals with a metallic luster were obtained using 2 mol% and 3 mol% excess Li content for feeds with a diameter of 10 mm and 13 mm, respectively, as shown in Figures 4(c) and 5(b). In contrast, for TSFZ growth using feeds with a Li content that was too high, rough and white crystal surfaces appeared during crystal growth. The reason for the appearance of a white crystal surface is the deposition of $Li_2O$ on the crystal surface during growth, as shown in Figs. 4(a) and 5(a). In addition, during the growth of $LiCoO_2$ crystals using a feed with too low Li content, contact between the feed rod and grown crystal frequently occurred periodically, creating instability in the molten zone. As a result, the grown crystals had a rough surface and cracks, as shown in Fig. 5(c). Fig. 6 shows SEM images of the insides at a rough and metallic luster surface parts in the grown crystal. Many voids and inclusions of cobalt oxide were observed at the inside of the rough surface part whereas the inside of the luster surface part had no inclusion. The origin of voids and inclusions in the grown crystals may be related with a temperature fluctuation and a constitutional supercooling near the growth interface due to operation to avoid contact between the feed rod and grown crystal. When contact between the feed rod and grown crystal occurs during TSFZ growth, the lamp power and the gap between the feed rod and grown crystals are adjusted to stabilize the molten zone. This operation results in a temperature fluctuation and a constitutional supercooling near the growth interface. As the results, inclusions of cobalt oxide with a high melting temperature deposited in the grown crystals by the constitutional supercooling, and the bubbles in the molten zone were incorporated as voids into the grown crystals due to the temperature fluctuation.

Fig.7 shows relationship between the excess Li content in the feed and the required lamp power. The reason for the deposition of excess $Li_2O$ and the instability in the molten zone was strongly related to the high Li evaporation during the TSFZ growth. The high lamp power enhanced Li evaporation from the molten zone. In our



Fig.4  As-grown crystals of $LiCoO_2$ of 10 mm in diameter grown at various excess Li content of feed (a) 5 mol%, (b) 3 mol%, (c) 2 mol% using solvent amount of 2.5 g, (d) 2 mol% using 3.0 g solvent.
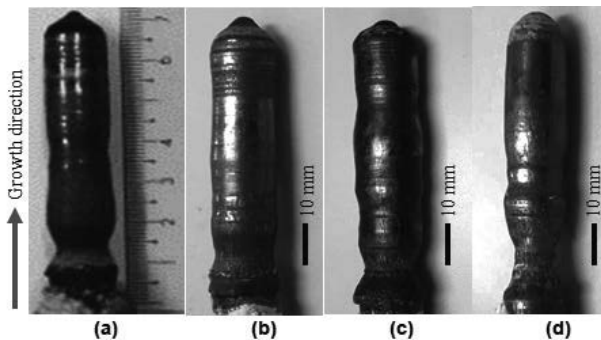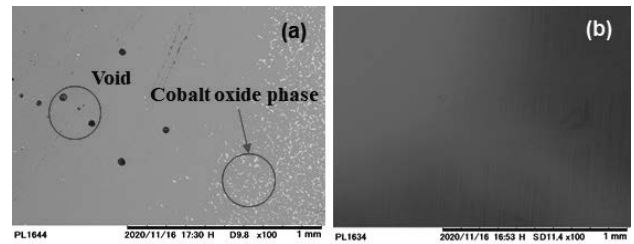


Fig.5  Photographs of $LiCoO_2$ crystals with a diameter of 13 mm grown at various excess Li contents in the feed (a) 5 mol%, (b) 3 mol%, (c) 2 mol% using a solvent amount of 4.9 g, (d) 3 mol% using 5.8 g solvent.
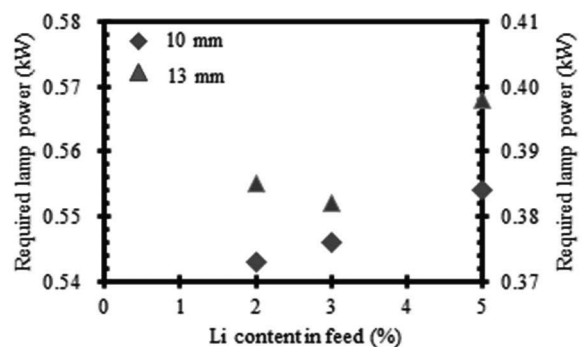


Fig.7  Relationship between excess Li content in the feed and required lamp power.

experiment, the Li component evaporated from the molten zone deposited onto the quartz tube surrounding the crystal growth region. The quartz tube with the deposited $Li_2O$ behaved as an obstacle for transmitting the effective heat in the molten zone during growth. As a consequence, contact occurred frequently, and the lamp power increased. The amount of Li component deposited onto the quartz tube increases with increasing the lamp power and excess Li content in the feed for the TSFZ growth of 10 mm and 13 mm crystals as shown in Figs. 8 and 9. Therefore, the growth results imply that the optimum excess Li content from the stoichiometric feed is an important parameter for the successful growth of large-diameter single crystals of $LiCoO_2$, avoiding the contact problem between the feed rod and grown crystals during TSFZ growth. The minimum Li evaporation is consistent with the lowest lamp power required for crystal growth as shown in Fig.7. Fig.10 shows a plot of the
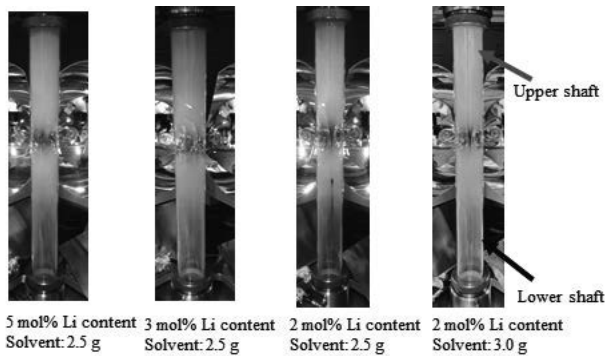


Fig.8 Quartz tubes after the growth of $LiCoO_2$ single crystals of 10 mm in diameter at different Li- excess solvent amount. White lithium oxide was deposited on the inner surface of the quartz tube.
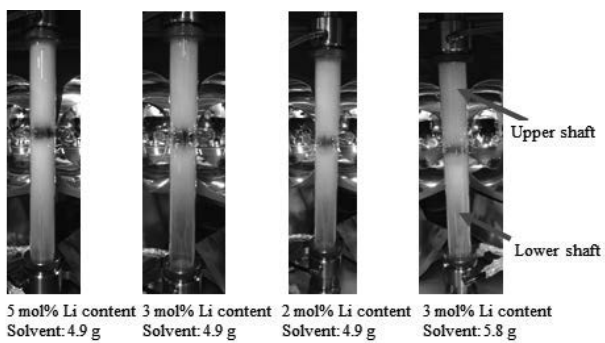


Fig.9 Quartz tubes after the growth of $LiCoO_2$ single crystals of 13 mm in diameter at different Li- excess solvent amount. White lithium oxide was deposited on the inner surface of the quartz tube.
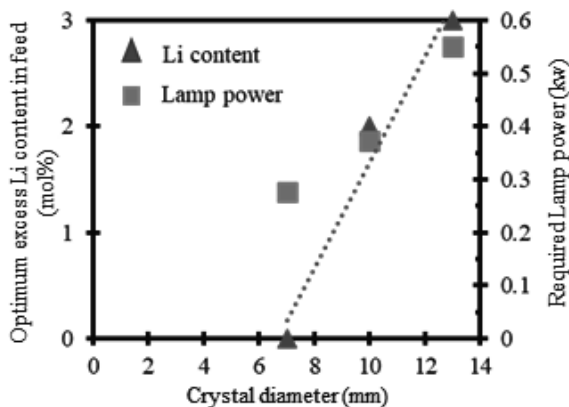


Fig.10 Relationship among the optimum excess Li content in the feed, crystal diameter and required lamp power.

relationship among the optimum excess Li content in the feed, crystal diameter and required lamp power for crystal growth the optimum raw materials based on the data of Fig.7.

This relation indicates that the excess Li content from the stoichiometric composition is linear with respect to the diameter of the grown crystal. Furthermore, the required lamp power increased considerably with increasing the crystal diameter. In special, the required lamp power for the crystal diameter of 13 mm was approximately twice time higher than that for 7 mm. Therefore, addition of a small amount of $Li_2O$ into the $LiCoO_2$ stoichiometric feeds is effective on stability of the molten zone when the crystal diameter exceeds 7 mm.

The amount of solvent also is effective on stability of the molten zone and the crystal quality for the TSFZ growth of $LiCoO_2$ large diameter crystals. The optimum amount of the solvent for crystal diameter of 10 and 13 mm were determined to be 2.5 g and 4.9 g, respectively as shown in Figs. 4(c) and 5(b). When the amount of the solvent was larger than the optimum amount, the melting zone became long and the melt easily drips, so that the melt was slightly solidified on the crystal surface and the crystal surface was roughened, as shown in Figs. 4(d) and 5(d). The relationship between the optimum amount of solvent and the crystal diameter is shown in Fig.11. The optimum amount of solvent was linearly related to the square of the crystal diameter. If the length of the molten zone is corresponding to shape and size of the lamp filament, the volume of the molten zone is proportional to square of the crystal diameter. Therefore, this result is consistent with the geometric consideration. This implies that the amount of solvent can be estimated from this linear relationship to grow $LiCoO_2$ single crystals with larger diameter.
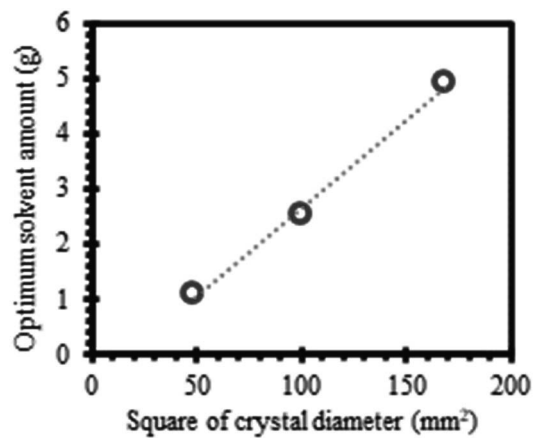


Fig.11 Relationship between optimum solvent amount and crystal diameter.

## 4. Conclusions

The effects of excess Li content in the feed, the amount of solvent and the filament shape of the heating lamps on the growth of large-diameter single crystals of $LiCoO_2$ were investigated by the TSFZ technique using a tilting-mirror-type image furnace. The stability of the molten zone during growth is an important factor in increasing the crystal diameter, which was significantly affected by the excess Li content, the feed composition, the amount of solvent and the filament shape of the heating lamp. The cylindrical-type filament was effective in maintaining the optimum molten zone length for the growth of large single crystals of $LiCoO_2$ up to 13 mm in diameter. For the 13 mm diameter single crystal growth, a stabilized molten zone avoiding the contact problem was found at the optimum amount of solvent of 4.9 g using a 3 mol% excess Li content feed composition. The required lamp power for crystal growth and amount of Li evaporation from the molten zone during growth was

lowest under these optimized growth conditions. A linear relationship between the optimum amount of solvent and the square of the crystal diameter was observed during the growth of large-diameter single crystals of $LiCoO_2$. Research into the growth of 13 mm (1/2 inch) diameter single crystal $LiCoO_2$ cathodes is applicable in the industrial applications of LIBs for the further development of next generation all solid state LIBs.

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