

Lowering the sintering temperature of LiCoO₂ using LiOH aqueous solution

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ABSTRACT

For realizing oxide-based all-solid-state lithium-ion batteries, lowering sintering temperature of LiCoO_2 cathode during battery fabrication is important subject to prevent undesired chemical reaction with other constituent substances. Here we report that the addition of LiOH aqueous solution to the LiCoO_2 powder upon sintering improves the battery performance. Comparative study for the samples with and without LiOH solution, and with pure water by *in situ* transmission electron microscopy reveals that the liquid phase appears at much lower temperatures for the sample with the LiOH addition that improves the connectivity of LiCoO_2 particles.

1. Introduction

Li ion batteries [1] are the most important energy storage devices that drive a variety of applications from mobile devices to mobility vehicles [2]. With the rise of environmental issues, their importance has never been greater [3]. To improve their energy densities and safety, realization of all-solid-state lithium-ion batteries is strongly desired [4]. However, their performance is still poor for various reasons. The main obstacles are the interfacial resistance of hetero-interfaces, such as electrolyte and active materials, and homo-interfaces i.e., grain boundaries of solid electrolyte and active material[5]. In comparison to sulfide all-solid-state batteries [6, 7], the problem is more prominent for the oxide all-solid-state batteries [8, 9], where the ceramic solid electrolytes need to be combined with active

materials by sintering because of their very poor plasticity. Increasing the sintering temperature improves the connectivity of homo-interfaces, but it may also promote unfavorable chemical reactions at the hetero-interfaces between electrolytes and active materials, resulting in the poor Li ion conductivity [10-12]. Therefore, various routes to lowering the sintering temperature have been explored. For example, Ohta *et al.* reported that addition of Li_3BO_3 and CaO can significantly lower the sintering temperature of Nb-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ to 790 °C[13] while keeping its lithium ion conductivity comparable to those sintered at high temperature (1000 to 1200 °C), and Watanabe *et al.* reported that densification of $\text{Li}_6\text{La}_3\text{ZrTaO}_{12}$ was achieved at 775 °C by the addition of Bi[14].

To boost the performance of the battery, one also needs to improve the connectivity of homo-interfaces in active material in addition to electrolyte particle. In general, LiCoO_2 , the most widely used cathode material, is often ground to fine powder prior to sintering with solid electrolytes to improve the connectivity, but the performance is still unsatisfactory, and this may partly be due to the insufficient connectivity of homo-interfaces of LiCoO_2 .

Recently, low-temperature production of LiCoO_2 using hydrothermal reactions has been reported[15], in which the appearance of the liquid phase enhances the reactions. The idea of using a hydroxide with low melting temperature should also work for improving the connection between LiCoO_2 particles.

In this paper, we report that the addition of LiOH aqueous solution to the LiCoO_2 powder applied on

Li_{6.6}La₃Zr_{1.5}Ta_{0.4}O₁₂ (LLZT) surface upon sintering improves the charge-discharge characteristics. *In situ* transmission electron microscopy (TEM) observation of sintering process reveals that with LiOH aqueous solution, appearance of liquid phase improves the connection between particles at much lower temperatures than those with pure water and without any additives.

2. Experimental

Charge-discharge tests were performed for the battery cells consisting of mixed LiCoO₂ and Li_{6.6}La₃Zr_{1.5}Ta_{0.4}O₁₂ (LLZT) power cathode, LLZT electrolyte, and Li foil anode. The cathode layer was prepared by mixing LiCoO₂ powder (Toshiba Manufacturing Co. Ltd.) and LLZT electrolyte particles (Toshiba Manufacturing Co. Ltd.) in a weight ratio of 5.4:5.05, which corresponds to a volume ratio of 1:1. The resultant weight percentage of LiCoO₂ in the mixture is 48.3%. The mixture was applied over the entire surface of a 1 cm square substrate (Toshiba Manufacturing Co. Ltd.), with a thickness of 0.5 mm. Before the application, a 23-nm-thick metal Ta is coated on the LLZT substrate and heat-treated at 700 °C for 2 hours in oxygen atmosphere. Preliminary experimental results indicate that interposing a controlled thickness of Ta reduces resistance and improves cycling performance.

Prior to heat treatment, a droplet (10 µL) of saturated LiOH aqueous solution was placed to the one of the cells, and 10 µL of pure water was added to another cell for comparison. The remaining cell was

heat treated without any liquid. The LiCoO₂ contents of those cells were 0.46 mg, 0.51 mg, and 0.51 mg, respectively and this corresponds to the loading density of 0.46mg/cm², 0.51mg/cm², and 0.51mg/cm², respectively. A saturated LiOH aqueous solution with a concentration of 5.3 mol/L was used. Addition of 10 μL of this solution corresponds to 5.3 x 10⁻⁶ mol. The LiCoO₂ contents of the cells were 0.46 mg for LiOH aqueous addition, thus, the molar ratios of LiOH to LiCoO₂ was 0.89.

After the heat treatment, an indium layer with 5.7 nm in thickness was deposited on the anode side by DC magnetron sputtering, and a Li foil was attached by heating at 220 °C for 30 minutes.

In situ TEM observations were conducted using a heating holder (Fusion, Protochips Co. Ltd.). The holder is equipped with a micro-electromechanical system (MEMS) heating chip coated with silicon nitride membrane. Two types of chips were used: with and without carbon supporting films over the holes. LiCoO₂ particles were ground in a mortar, suspended in a saturated LiOH aqueous solution and dispersed on the heating chip. The chip was dried at 130 °C for 10 minutes before observations. Samples dispersed with and without pure water were also observed for comparison.

TEM, Scanning TEM (STEM), and electron energy-loss spectroscopy (EELS) observations were performed using a JEOL JEM-ARM200F spherical aberration-corrected microscope equipped with a Gatan Quantum camera. For the observation of deposit, The LiOH-saturated aqueous solution was diluted 10,000 times and drop-cast onto the carbon grid.

3. Results

3.1 Comparison of charge-discharge profiles

Fig. 1 shows charge-discharge profiles of the cells sintered with (green) and without (blue) LiOH aqueous solution, and with pure water (red). The rate was set to 0.1 C. The LiOH-mediated cell (green) exhibited a much larger capacity in comparison to the cell without the addition of LiOH solution (blue). In contrast, the capacity of the cell with the addition of water significantly decreased (red). This implies that LiOH aqueous solution improves the connectivity of hetero- and homo-interfaces between LiCoO₂ particles and/or LiCoO₂ and LLZT particles, while the water treatment induces adverse effects. Hence, LiOH is a key additive that improves the capacity of the cell.

3.2 TEM observations of LiOH deposits

The role of LiOH aqueous solution in the sintering process was elucidated by TEM. First, the deposits of LiOH were observed by dispersing only a LiOH solution onto a TEM grid. To make deposits with appropriate thickness for EELS observations, diluted solution was used, and the grid was dried under air at 130 °C for 10 minutes. From the diluted LiOH solutions, deposits with various sizes were formed as shown in Fig. 2(a). The edge of the deposits appears as aggregation of small platelets that are in crystalline state assignable to Li₂CO₃ as evident by diffraction pattern shown in Fig. 2(b). The EELS

feature near the Li-K edge (Supporting information) resembles the Li_2CO_3 spectrum. [16] Those results indicate that the deposits of LiOH were completely changed to Li_2CO_3 . Because a small amount of diluted LiOH solution was used, the resulting LiOH might be completely reacted with CO_2 in air during the drying process to form the Li_2CO_3 crystalline deposits.

3.3 *In situ* observation of sintering process of LiCoO_2 with LiOH additives

Sintering with LiOH additives was also investigated by *in situ* TEM. Fig. 3 shows in-focus (a) and defocused (b) images of LiCoO_2 particles that were suspended in a saturated LiOH aqueous solution and dispersed on the heating chip. Light-element compounds such as LiOH and Li_2CO_3 generate a small phase change to the incident electrons; hence they are almost invisible in the in-focus (Fig. 3(a)) but certainly appear in the defocused image (Fig. 3(b)). In contrast to the deposits from the diluted aqueous solution (Fig. 2), deposits are in amorphous phase and filling the space between particles. These deposits were generally thicker than those observed in the previous section and may be a mixture of LiOH and Li_2CO_3 . It is known that the formation of LiOH- Li_2CO_3 eutectics lowers the melting temperature [17], and melted liquid phase should enhance the inter-diffusion of LiCoO_2 . Thus, the formation of Li_2CO_3 should enhance sintering.

Fig. 4 illustrates *in situ* TEM images measured at different temperatures. The corresponding video is available in the supporting information (1. LCO with LOH_RT to 600 deg.mp4). At around 200 °C, a

“sea-island” structure appeared in the LiOH deposit region (the arrow in Fig 4 (b)), and the pattern grew and coarsened as temperature increased (the arrow in Fig. 4(c)). This is probably due to the melting of LiOH. LiCoO₂ particles started to melt at around 340 °C, and almost completely melted by 400 °C. Since the liquid phase of LiOH appears first, the melting of LiCoO₂ should rather be considered as "dissolving.". At around 575 °C, the boundaries between LiOH and LiCoO₂ disappeared, and a single molten phase was formed at 600 °C. After keeping the sample at 600 °C, some areas turned to show diffraction contrast indicating those areas changed into crystalline state as indicated by an arrow in Fig. 4(f). EDS measurement performed later from those areas at room temperature (Fig. 5) revealed that those crystalline areas are rich in Co and likely represent LiCoO₂.

These *in situ* observations of sintering process were performed using a heating chip with carbon supporting film. Similar results were obtained without the film and are presented in the supporting information (7. LCO with LiOH with no carbon film RT to 600 deg .mp4.) confirming that the above-mentioned phenomena such as a single molten phase formed below 600 °C, was not affected by the carbon support.

3.4 *In situ* observation sintering process of LiCoO₂ with pure water

In situ observations were also conducted for particles dispersed using pure water. The results are summarized in Fig. 6, and the corresponding video is available in supporting information (2. LCO

with water_RT to 600 deg.mp4, 3. LCO with water 600 deg to 750 deg.mp4). In contrast to heating with LiOH additives, no noticeable change occurred until 750 °C. Around 750°C, however, the particles suddenly became round, the connections between them became thicker, and some small particles were merged to form larger particles within about 10 seconds (Fig. 6 (c)). After that, the image has stabilized. Although some small particles were absorbed, the particles were, as a whole, not melted, and preserved their original configurations meaning the connection between particles becomes thicker by surface and volume diffusion. Therefore, the observed process was likely a solid phase reaction. The temperature of 750 °C (~1020 K) is 300 °C lower than the melting point of pure LiCoO₂ (1130 °C or ~1400 K), which is a rather common difference for sintering.

3.5 *In situ* observation of sintering process of mechanically dispersed LiCoO₂

Lastly, to investigate the effect of pure water and LiOH solution on sintering process, additive-free LiCoO₂ particles were mechanically dispersed on a heating chip and observed *in situ* TEM. When a heating chip with carbon supporting film was used, LiCoO₂ reacts with the carbon film to produce metallic Co. This may be because the heating was performed under vacuum, so that LiCoO₂ was reduced by the carbon film upon heating and CO₂ was formed. The corresponding video is available in supporting information (8. LCO only on carbon film RT to 600 deg.mp4).

Thus, a heating chip without carbon supporting film was used in the present experiment as shown in Fig. 7. The corresponding video can be found in supporting information (4. LCO only with no carbon film RT to 600 deg.mp4, 5. LCO only with no carbon film 600 to 700 deg.mp4, 6. LCO only with no carbon film 700 to 750 deg.mp4). Unlike the previous two experiments where the rounding started at 340 °C and 750 °C, the rounding of the particles started at around 600 °C and gradually progressed up to 700 °C. At around 740 °C, the coarsening started, and a single large grain was formed at around 750 °C. As compared with the water addition case, the connection is more continuous, and there is no trace of original particles in the merged grain. This result agrees with the fact that the charge-discharge capacities in Figure 1 are higher for LiCoO₂ with LiOH, without LiOH, and with water in that order.

4. Discussion

As demonstrated by Liang *et al.* [15], the eutectic effect of LiOH and Li₂CO₃ lithium precursors can lower the solid-state reaction temperature. In the present study, although the samples for the charge-discharge test were heat-treated in oxygen, since the samples were handled in the air, some part of LiOH might be reacted with CO₂ to form Li₂CO₃, forming a eutectic binary phase with even lower melting temperature.

In the *in situ* observations of sintering process, the observations were conducted for relatively small

LiCoO₂ particles that were being heated in vacuum. Although the heating rate in the TEM heating experiment is set faster compared to the heating rate in a tube furnace for the bulk, we believe that the particles being observed reach a sufficiently uniform temperature at each temperature range because the particle size is very small relative to the sample holder acting as a thermal bath. As for the atmosphere, we have confirmed that a functioning battery can be fabricated by heat treatment under an Ar atmosphere (i.e., oxygen-free). Since the temperature at which the liquid phase appears during in-situ TEM observation matches the temperature at which battery performance improves in bulk cells, we believe that the mechanism by which LiOH generates a liquid phase, thereby promoting the sintering of LiCoO₂, occurs similarly in bulk batteries, and the in-situ experiment accurately replicates the behavior of bulk batteries.

The melting temperature of the LiOH-Li₂CO₃ depends on the ratio of these compounds [17] . In our experiment, sintering was performed in pure oxygen, and hence precise control of the ratio was not possible. However, if we could sinter the mixture in a controlled atmosphere and fine-tune the ratio upon sintering, we might be able to further lower the sintering temperature.

In this work, we focused on the effect of LiOH on the sintering between LiCoO₂ particles. However, it is quite possible that LiOH also improve the connection between LiCoO₂/LLZT particles and LLZT/LLZT particles. We intend to further investigate the effect of LiOH on the sinterability between LLZT particles in future

199

200 **5. Conclusions**

201 The addition of LiOH aqueous solution can improve the connection of LiCoO₂ particles at much lower
202 sintering temperatures, resulting in greatly improved charge-discharge performance in comparison
203 with the samples without LiOH solution and with pure water. *In situ* observations of sintering process
204 reveal that liquid phase appears at much lower temperatures, which improves the connection of
205 LiCoO₂ particles. The lowering of the sintering temperature widens the process condition when
206 fabricating batteries by suppressing side reactions between cathode and electrolyte materials. Hence
207 these results may be useful for the development of all-solid base oxide batteries.

208

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214 **References**

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241

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Figure captions

Fig.1. Charge-discharge profiles of the cells sintered with (green) and without (blue) LiOH aqueous solution, and with pure water (red). The performance improves for the cell with LiOH aqueous (green), while it degrades with water (red).

Fig. 2. (a) Deposits formed from diluted LiOH aqueous solution dispersed onto a carbon grid. (b) Diffraction pattern from a deposit that can be indexed as Li_2CO_3 .

Fig. 3. TEM images of LiCoO_2 particles that were suspended in a saturated LiOH aqueous solution and dispersed on the heating chip: (a) in focus, and (b) defocused.

Fig. 4. In situ heating result of LiCoO_2 with LiOH deposits. The arrows in (b) and (c) indicate the LiOH deposit region where “sea-island” structure appears. The arrow in (f) indicates a crystalline area appeared in melted region.

Fig. 5. EDS map of LiCoO_2 with LiOH deposits heated up to 600 °C. Green, red, and blue correspond to cobalt, oxygen, and carbon, respectively.

261

262 Fig. 6. *In situ* observation result of LiCoO_2 particles dispersed with pure water. The sintering
263 suddenly progresses at around 750°C at which connection between particles becomes thicker while
264 keeping their positions.

265

266 Fig. 7. *In situ* observation result of LiCoO_2 particles dispersed mechanically without using LiOH
267 solution nor pure water. The rounding of particle shapes started around 600°C and gradually
268 progressed up to 700°C .

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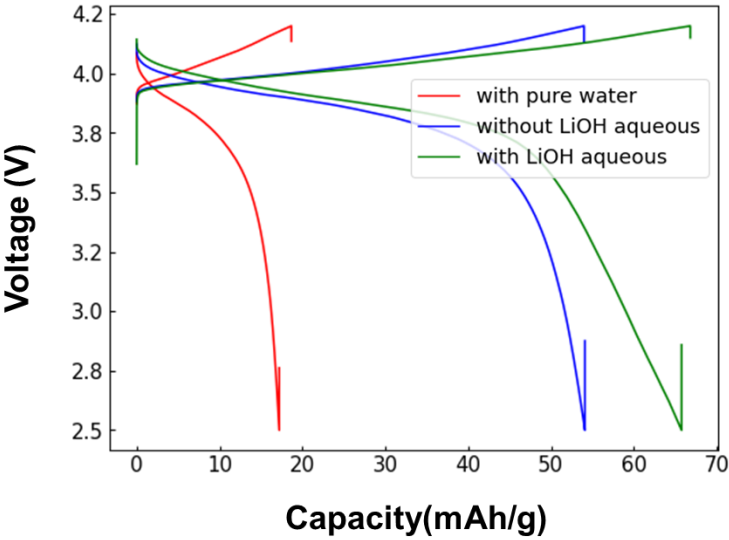


Fig. 1. Charge-discharge profiles of the cells sintered with (green) and without (blue) LiOH aqueous solution, and with pure water (red). The performance improves for the cell with LiOH aqueous (green), while it degrades with water (red).

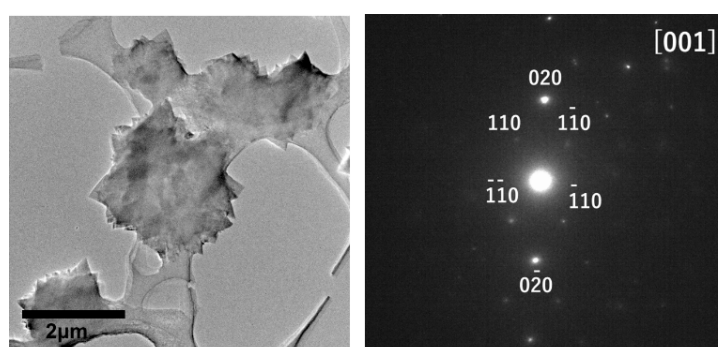


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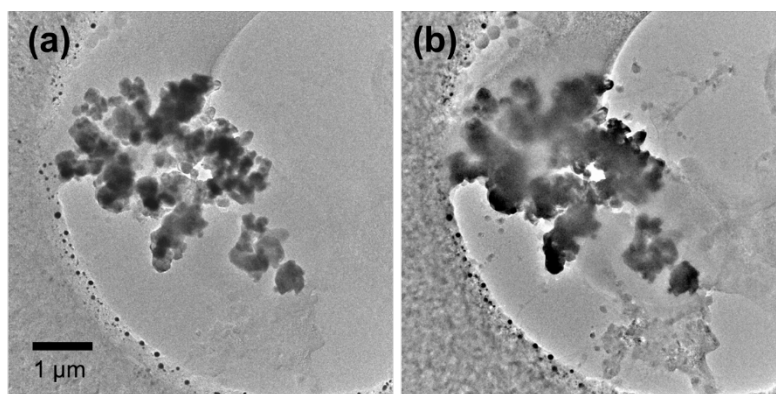


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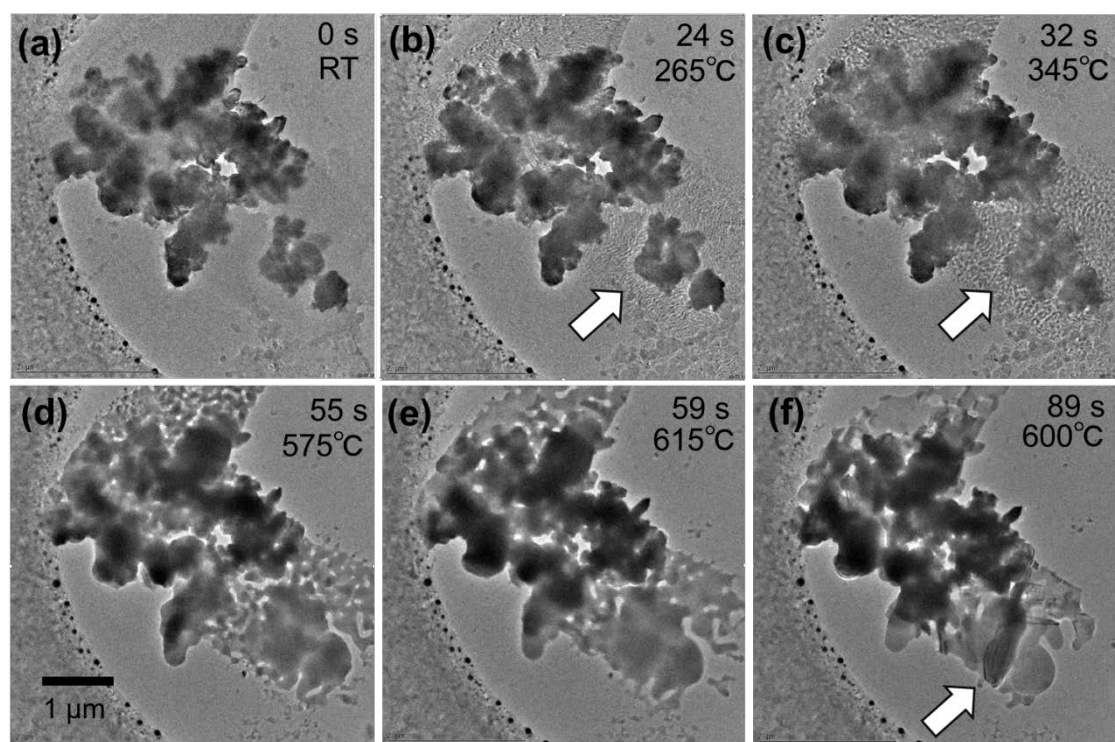


Fig. 4. *In situ* heating result of LiCoO_2 with LiOH deposits. The arrows in (b) and (c) indicate the LiOH deposit region where "sea-island" structure appears. The arrow in (f) indicates a crystalline area appeared in melted region.

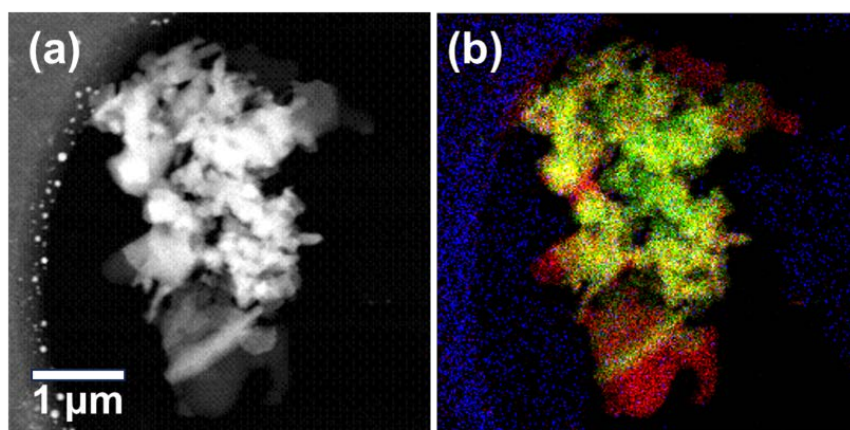


Fig. 5. STEM (a) and EDS map (b) of LiCoO_2 with LiOH deposits heated up to 600 °C. Green, red, and blue correspond to cobalt, oxygen, and carbon, respectively.

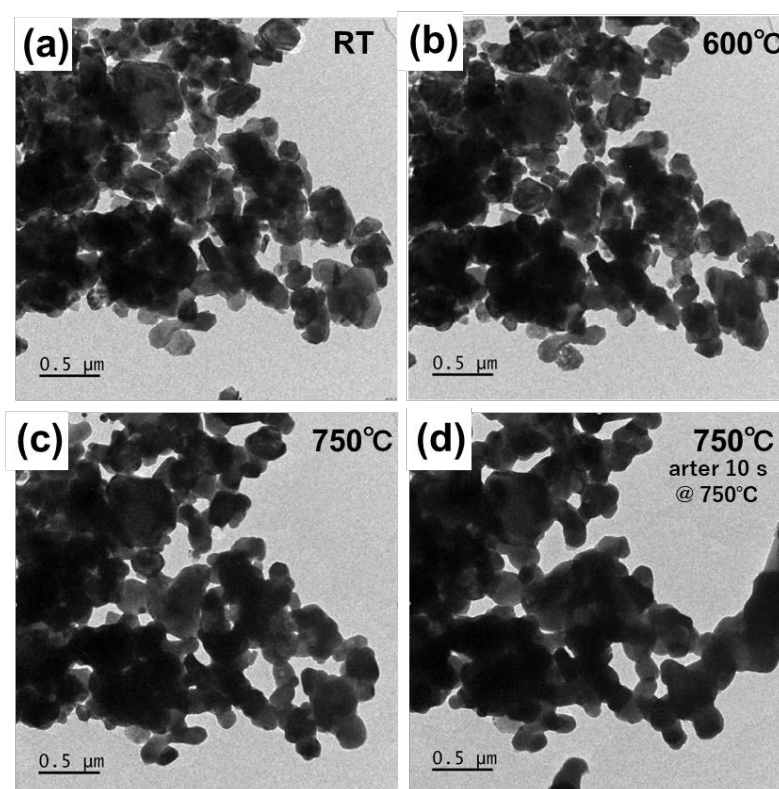


Fig. 6. *In situ* observation result of LiCoO_2 particles dispersed with pure water. The sintering suddenly progresses at around 750°C at which connection between particles becomes thicker while keeping their positions.

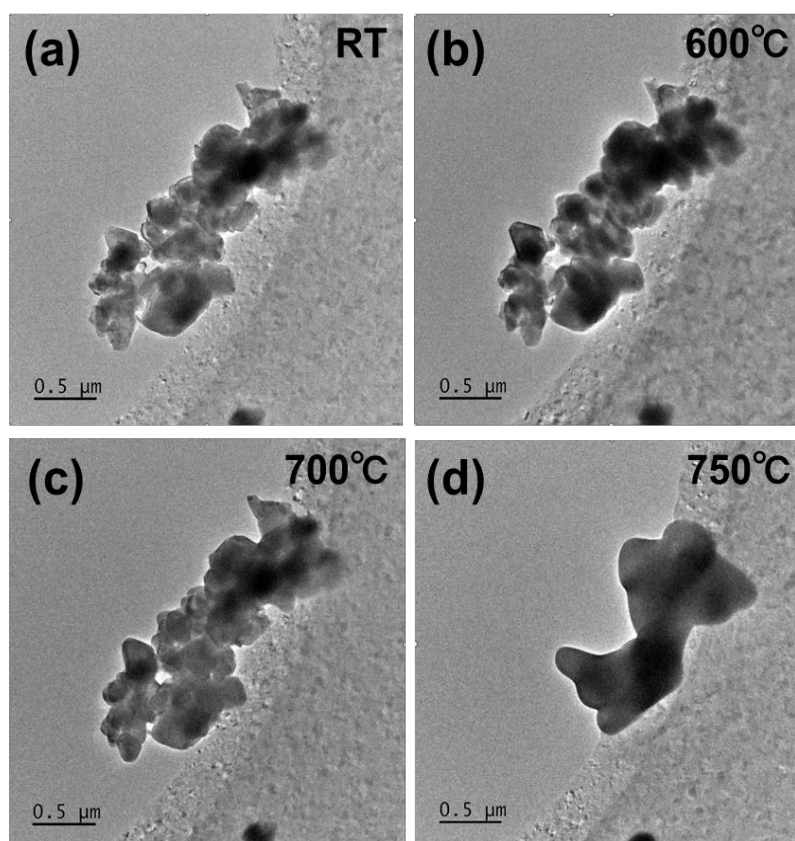


Fig. 7. *In situ* observation result of LiCoO₂ particles dispersed mechanically without using LiOH solution nor pure water. The rounding of particle shapes started around 600°C and gradually progressed up to 700 °C.