Formation of Non-Aggregated Li$_4$Ti$_5$O$_{12}$ Particles in a Flame Reactor

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Received 3 June 2016
Accepted 13 October 2016

Abstract We studied the formation of non-aggregated Li$_4$Ti$_5$O$_{12}$ particles by reaction between lithium nitrate and titanium tetraisopropoxide in a methane/oxygen coflow diffusion-flame reactor. We obtained the powder consisting of phase-pure Li$_4$Ti$_5$O$_{12}$ particles after calcination at 1,073 K. The particles produced in the flame reaction from the spray solution contained an excess amount of lithium corresponding to 25% of the stoichiometric amount. A change in the proportion of virtually non-aggregated particles in TEM images was observed using a rapid cooling of the entire flame aerosol by blowing with cold quenching gas of Ar followed by supercooling in a Laval nozzle placed above the flame. The proportion of non-aggregates was 28% for the particles produced without any cooling steps. When the flame aerosol was supercooled in the Laval nozzle after blowing with 203 K Ar quenching gas, the proportion of non-aggregates was as large as 88%. Thus, rapid cooling in the region of the flame tip is quite effective for preventing particle aggregation.

Keywords: Lithium Titanate Particles, Non-aggregates, Supersonic Flow, Laval Nozzle.

1. Introduction

Lithium-ion rechargeable batteries are needed as high-energy storage devices for electric vehicles, mobile devices, and storage systems. Spinel lithium titanate (Li$_4$Ti$_5$O$_{12}$) offers good reversibility of Li-ion intercalation and de-intercalation and exhibits no structural change during charge-discharge cycling as an anode material for Li-ion batteries (Ohzuku et al., 1995; Zaghib et al., 1999; Takai et al., 1999; Ju et al., 2010; Li et al., 2011). Recently there has been intense interest in nanostructured electrode materials by virtue of their short diffusion lengths and more active surface areas for Li$^+$. For these reasons, the preparation of nanosized Li$_4$Ti$_5$O$_{12}$ powder has been well studied (Guerfi et al., 2003; Ge et al., 2008; Wang et al., 2009; Bresser et al., 2012) by using various solid-state and liquid-solution methods. However, the preparation of Li$_4$Ti$_5$O$_{12}$ powders via gas-phase reaction methods has been much less well studied (Ernst et al., 2007; Tang et al., 2008). In these studies, the obtained Li$_4$Ti$_5$O$_{12}$ powders contained aggregated particles because there was no means to prevent necking between particles. Due to this aggregation, the particles often lose their uniform nanosized shape and, as a result, their interesting properties.

In this study, we apply a technique we developed previously (Okada et al., 2011), for the rapid cooling of particles formed in a flame reactor by supercooling in a Laval nozzle placed above the flame, in order to produce non-aggregated Li$_4$Ti$_5$O$_{12}$ particles. We quantitatively investigate the degree of non-aggregation of the Li$_4$Ti$_5$O$_{12}$ particles produced in a coflow diffusion flame reactor under various conditions.

2. Experimental

Fig. 1 shows our experimental setup. A coflow diffusion burner consisting of four concentric stainless steel tubes was used. The inner diameters of the tubes were 4.35, 8.0, 11.0, and 14.0 mm. The tube wall thickness was 1.0 mm. An argon stream of 0.5 L/min carrying precursor solution from the nebulizer flowed through the centermost tube of the burner, while 1.3 L/min of argon, a mixture of 0.8 L/min of methane and 0.5 L/min of oxygen, and 1.5 L/min of oxygen flowed through the second, third, and fourth tubes of the burner, respectively. The length of the flame was approximately
145 mm. The argon stream flowing through the second tube was used to increase the height of the flame to ensure the reactants had a long residence time.

Fig. 1 also shows the details of the quenching gas device and Laval nozzle. The quenching gas ring had eight nozzles through which the Ar quenching gas exited. The nozzles were pointing upward at an angle of 20°. Each nozzle had an angular offset of 10° relative to the center axis. The quenching gas ring was positioned so that the quenching gas blew on the tip of the flame. The cold quenching gas of 12.5 L/min Ar at approximately 203 K was prepared by allowing it to flow through a methanol slush bath cooled at 176 K.

The Laval nozzle, with a throat diameter of 2.0 mm, was set at 152 mm downstream from the burner mouth. The pressures in the upstream and downstream regions of the Laval nozzle were maintained at 103 kPa and 20 kPa, respectively.

Lithium nitrate (LiNO₃) and titanium tetraisopropoxide (TTIP, Ti[OCH(CH₃)₂]₄) were chosen for the materials of the precursor solution. This solution, having a predetermined molar concentration, was made by dissolving these materials into ethanol (CH₃CH₂OH 99.5%). The solution was atomized with a 1.7 MHz ultrasonic spray generator with four vibrators. The atomized droplets were subsequently carried into the central tube of the burner by Ar carrier gas.

A portion of the synthesized particles were collected on a transmission electron microscopy (TEM) grid set in the tip of the deposition system for analysis, while the others were collected on a stainless steel cartridge filter. The deposition system was positioned approximately 280 mm downstream from the Laval nozzle.

The diameters and degrees of non-aggregation of more than about 200 particles obtained under each condition were analyzed by TEM (JEM-2010-K, Jeol Ltd., 100 kV). To improve the crystallinity of the particles and remove possible impurity phases, the as-synthesized powders obtained by flame spray pyrolysis were post-treated in a box furnace at 1,073 K for several hours in an air atmosphere. The crystal structures of the powders were investigated by X-ray diffractometry (XRD, RINT-TTRIII/RX, Rigaku Corp.) operating with Cu Kα radiation at room temperature.

3. Results and Discussion

Fig. 2(a) shows the X-ray diffraction spectrum of the as-synthesized powder prepared from a spray solution with a
molar ratio of LiNO₃ to TTIP of 4:5, which corresponds to the stoichiometric amount of Li₄Ti₅O₁₂, without any cooling steps. Compared with the XRD patterns of the several kinds of molecules shown in Fig. 2, the as-synthesized powder was found to be a mixture of Li₄Ti₅O₁₂, Li₂TiO₃, Li₂Ti₃O₇, anatase TiO₂, and rutile TiO₂. When we compared the heights of the peaks in Fig. 2(a), we supposed that Li₄Ti₅O₁₂ and rutile TiO₂ were major components.

We measured the lowest and highest temperatures in the flame at approximately 1,373 K and 1,673 K by using a thermocouple thermometer. It is known that TTIP and LiNO₃ react to form Li₂TiO₃, anatase TiO₂, and rutile TiO₂ in the region whose temperature is lower than 873 K (Mohammadi and Fray, 2010). In the region between 1,073 K and 1,173 K, the following reaction occurs (Shen et al., 2014).

\[
2\text{Li}_2\text{Ti}_3\text{O}_7 + 3\text{rutile TiO}_2 \rightarrow \text{Li}_4\text{Ti}_5\text{O}_{12} \quad (1)
\]

At a temperature higher than 1,230 K, the next reaction takes place (Zhu et al., 2013).

\[
\text{Li}_2\text{TiO}_3 + 2\text{rutile TiO}_2 \rightarrow \text{Li}_4\text{Ti}_5\text{O}_{12} \quad (2)
\]

Since the major area in our flame, excluding the boundary of the flame, was higher than 1,230 K, we can infer that Li₂Ti₃O₇ was produced as a major component by our experiment.

Fig. 2(b) and 2(c) show XRD spectra of the powders after calcination at 1,073 K for 4 hours and 12 hours, respectively. From Fig. 2(b), we found that the powder was a mixture of Li₂Ti₅O₁₂ and rutile TiO₂. After calcination for longer periods, such as 8 or 12 hours (shown in Fig. 2(c)), the small peak of rutile TiO₂ remained and the ratio of the peak height of Li₄Ti₅O₁₂ to that of rutile TiO₂ was almost unchanged.

Next, we synthesized powder from the spray solution with a molar ratio of LiNO₃ to TTIP of 1:1 without any cooling steps. The spray solution contained an excess amount of lithium that corresponds to 25% of the stoichiometric amount.

Fig. 3(a) shows an XRD spectrum of the as-synthesized powder. The figure shows that the powder was a mixture of Li₂Ti₅O₁₂, Li₂TiO₃, Li₂Ti₃O₇, anatase TiO₂, and rutile TiO₂. Fig. 3(b) shows an XRD spectrum of the powder after calcination.
calcination at 1,073 K for 12 hours. The figure indicates that the powder contained only Li$_4$Ti$_5$O$_{12}$. We found that the post-treatment produced phase-pure Li$_4$Ti$_5$O$_{12}$ powder.

In the post-treatment at 1,073 K, we understand that Li$_4$Ti$_5$O$_{12}$ was produced according to the following reactions (Zhang and Banfield, 2000; Hayashi and Hatano, 1994; Shen et al., 2014).

\[
\begin{align*}
\text{anatase } \text{TiO}_2 & \rightarrow \text{rutile } \text{TiO}_2 \\
2\text{Li}_2\text{Ti}_3\text{O}_7 & \rightarrow \text{Li}_4\text{Ti}_5\text{O}_{12} + \text{rutile } \text{TiO}_2 \\
2\text{Li}_2\text{TiO}_3 + 3\text{rutile } \text{TiO}_2 & \rightarrow \text{Li}_4\text{Ti}_5\text{O}_{12} 
\end{align*}
\]

When rutile TiO$_2$ and Li$_4$Ti$_5$O$_{12}$ remain after calcination as shown in Fig. 2(c), the rutile TiO$_2$ cannot disappear by any reactions in the calcination, because no more of Li$_2$TiO$_3$, which reacts with rutile TiO$_2$ in Eq. (5), exists.

Fig. 2(c) shows that a small amount of rutile TiO$_2$ remained, except for Li$_4$Ti$_5$O$_{12}$, in the product generated from the spray solution that contained Li atoms and Ti atoms with a number ratio of 4:5, corresponding to the stoichiometry of Li$_4$Ti$_5$O$_{12}$. From this, we presumed that Li atoms should become volatilized by the reactions in the flame and by the calcination. In fact, when the powder shown in Fig. 2(c) underwent a supplementary calcination at 1,473 K for 12 hours, the peak of Li$_4$Ti$_5$O$_{12}$ vanished and the peak of rutile TiO$_2$ remained only in the XRD spectrum.

From the fact that Li atoms became volatilized, we found that the spray solution must contain an excess amount of lithium. We understand that a powder consisting only of Li$_4$Ti$_5$O$_{12}$ could be produced from spray solution containing an excess amount of lithium corresponding to 25% of the stoichiometric amount, as shown in Fig. 3(b).

Fig. 4 shows a TEM image and the size distribution based on the number of as-synthesized particles produced without any cooling steps (Ar quenching gas blowing or use of the Laval nozzle). In the TEM images, we observed a coalescence of particles with unclear boundaries for each particle. The particles that had clear boundaries with all adjacent particles were distinguished from the particles that had one or more unclear boundaries with adjacent particles due to the necking between particles. The former was defined as non-aggregates, and the latter as aggregates. The proportion of non-aggregates was approximately 28%.

We understand that improvements in the degree of non-aggregation should depend on the cooling rate of the surface temperatures of particles (Okada et al., 2011 and Okada et al., 2014). We utilized the supercooling of the aerosol by adiabatic expansion in the Laval nozzle, the inlet of which was set approximately 7 mm below the tip of the flame. Fig. 5 shows a TEM image and the size distribution of the as-synthesized particles produced by quenching with blown Ar gas and with the Laval nozzle. The quenching gas Ar cooled at 203 K blew on the tip of the flame from the gas ring. The proportion of non-aggregates was as large as 88%. We obtained a high proportion of non-aggregates. We found that the supercooling of the aerosol accompanied by cold quenching gas in the Laval nozzle was quite efficient for the generation of non-aggregated particles. In addition, from the result that the size distribution of non-aggregates in Fig. 5 was sharper than that in Fig. 4, we found that the supercooling of the aerosol was efficient also for the growth of monodispersed particles. TEM observation after calcination at 1,073 K confirmed no changes in the size distribution of the particles.

The experimental results in our previous works (Okada et al., 2011 and Okada et al., 2014) indicated that not all the particles were cooled by the blowing of quenching gas and that some hot particles passed through the center of the aerosol flow from the flame to the Laval nozzle without
being cooled by mixing with the quenching gas. Let us assume that a part of the aerosol is introduced into the Laval nozzle without any cooling by collision with the quenching gas blow, and that the temperature of this aerosol at the inlet of the Laval nozzle is 1,373 K, which is the temperature of the flame. From the 20 kPa value of the gas pressure in the downstream region of the Laval nozzle and from the specific heat ratio of the aerosol, the lowest temperature of the gas in the Laval nozzle was estimated to be 716 K by the dependence of temperature and pressure on the Mach number of the gas in a steady-isentropic flow in the Laval nozzle (Liepmann and Roshko, 1957). The period of time when the gas passes from the inlet of the nozzle to the lowest temperature point in the nozzle was calculated to be approximately 0.2 ms. We understand that the particles underwent very rapid cooling in the Laval nozzle.

Fig. 5 TEM image and size distribution of particles produced with rapid cooling by jets of quenching gas and the Laval nozzle.

4. Conclusion

We successfully produced Li₄Ti₅O₁₂ powders by combining the methane flame reaction with calcination from the spray solution of a mixture of LiNO₃ and TTIP containing an excess amount of lithium corresponding to 25% of the stoichiometric amount.

We have investigated the proportions of non-aggregated particles produced. We found that the particles with sufficiently high degrees of non-aggregation, as large as 88%, could be produced with a system in which rapid cooling of the aerosol at the flame reactor exit is achieved by means of jets of quenching gas followed by supercooling in a Laval nozzle. The particles produced without any cooling steps had degrees of non-aggregation as low as 28%. We believe that this increase in the degree of non-aggregation is caused by the rapid cooling of the aerosol going out of the flame.

References

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