Drying Process of Positive Electrode Slurry of Li-Ion Battery Having Different Internal Structure

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Introduction

The cathode of Li-ion battery (LiB) consists of an active material (ex. lithium cobalt oxide, LCO), a conductive additive (ex. acetylene black, AB) and a binder (ex. polyvinylidene fluoride, PVdF). They are usually dispersed in a solvent (ex. 1-methyl-2-pyrrolidon, NMP) to produce slurry. Cathode is manufactured through the processes of coating, drying and pressing of the slurry. In order to utilize state-of-the-art materials, the manufacturing process of electrode need to be developed based not on try-and-error but on scientific knowledge. In general, battery performance is characterized by energy density, which is the amount of electricity can be stored in a unit volume or weight of battery cell. Roughly speaking, higher packing density of particulate material is required for higher energy density. Additionally, higher packing density means more frequent connection between materials, which reduces electrical resistance. Therefore, the formation process of packing structure of particulate materials during drying is urge to be clarified even for commercially available LiBs.

Active materials, such as LCO, for LiB have a significantly large capacity to store electron. However, they usually showed poor electrical conductivity. Therefore, it is indispensable to form the network structure of conductive additive particles, such as acetylene black AB, in electrode films in order to transport electron from the surface of electrode to the surface of active material. Many researchers pointed out that the preparation procedures significantly affect the electrical conductivity of electrode and battery performance [1-5], and it was proven in our group than the difference in the internal structure of cathode slurry with slurry preparation processes is reflected in the viscoelastic properties of the slurry [1]. However, the structural change in the drying process was still laid as a black-box. In the present study, we focused on the shrinking process of cathode slurry during drying and investigated the effects of the initial internal structure of slurry and drying temperature on the shrinking behavior of the coated cathode slurry. The results will depict the effect of the evaporation rate of solvent and the bridging structure of particulate materials on the behavior of particle packing process, and the findings must be helpful for obtaining high packing density electrode.

Experiment

Material and slurry preparation

The cathode slurry in the present study is composed of active materials (LCO, 6.8µm), conductive additive (AB, 35nm), binder (PVdF), and solvent (NMP). PVdF was added to the particulate materials as 12wt% NMP solution, and finally diluted to 8wt% with the addition of NMP. The volume fraction of LCO and AB particles in the final slurry was 19.5 and 2.0vol%, respectively.

Three types of slurry preparation processes have been adopt. The flowchart of slurry preparation processes are shown in Fig.1. As the simplest process, the mixture of all materials were dispersed 6 times, which is referred as "in-whole" process. On the contrary, all other than NMP for dilution was firstly mixed and dispersed, and then the dispersion and addition of a 1/5 portion of NMP were repeated 5 times, which is referred as "in-parts" process. The repetition of dispersion was same at 6 times for both processes. In the last "2-step" process, dilute AB slurry, which is the cathode slurry excluding LCO particles, was first prepared with sufficient repetition of dispersion. The full portion of LCO particles were added to sufficiently dispersed AB slurry and then the dispersion was repeated for 8times. In each dispersion process, a planetary mixer was used and operated at 2000rpm for 3min.

The rheological properties of the slurry under preparation or after preparation were measured using a stress-controlled rheometer at room temperature with a cone-plate fixture (50mm) to characterize the difference in the internal structure of slurry.

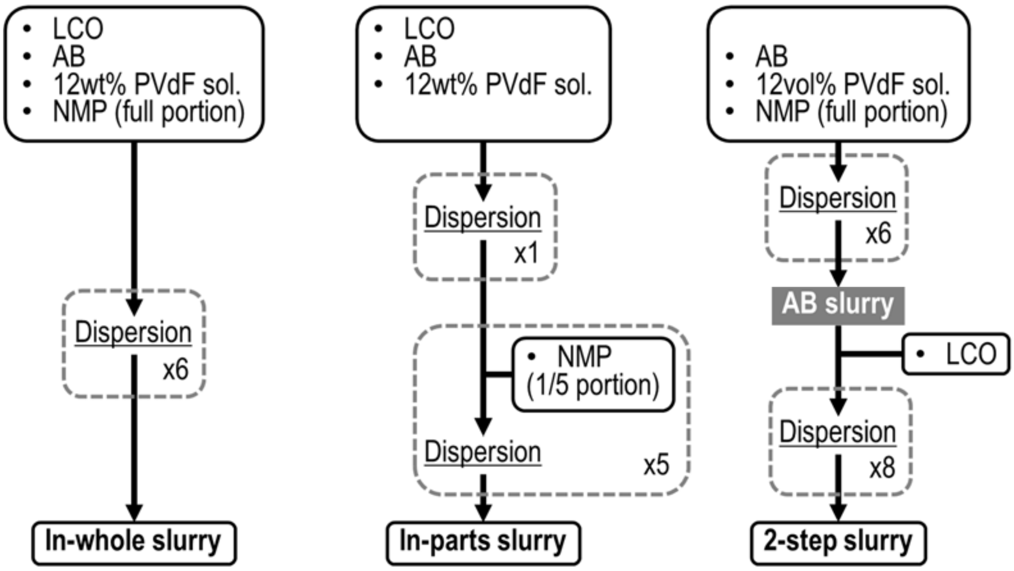


Fig.1 Preparation process of cathode slurry

Evaluation of film shrinking process with drying

Cathode slurry was coated on an aluminum sheet, which adhered on a glass plate, using a doctor blade having the coating gap of 200μm at the coating speed of 6 mm/s. The slurry coated glass plate was placed on a glass heater, the surface temperature of which was maintained at 45, 80 and 100°C. The coated slurry and glass heater was placed in the temperature and humidity controlled chamber at 25° C and 50% RH. The decreasing trend of the coated film thickness were measured using a laser displacement sensor at the interval of 1s by the similar manner to our previous studies [6][7]. The initial thickness of the coated film was calculated from the weight of the coated film and the density of slurry.

Results and Discussion

Rheological interpretation of internal structure of cathode slurry

For the purpose to understand the internal structure formed in a cathode slurry, the rheological properties of cathode slurry have been investigated. First of all, the rheological properties of components of the cathode slurry was studied. The composition of slurries are listed in Table 1. The apparent viscosity as a function of shear rate and the elastic moduli as functions of frequency were shown in Fig. 2 for AB slurry, LCO slurry and 8wt% PVdF solution. AB and LCO slurries were cathode slurries excluding LCO or AB particles. The mixture of 8wt% PVdF solution with AB and LCO particles were repeatedly dispersed until obtaining steady state in terms of rheological properties. LCO slurry almost attained steady state even after the 1st dispersion, while AB slurry showed gradual decrease in viscosity and elastic moduli, and required at least 6times of dispersion.

Table 1 Composition of slurry

	Weight ratio				Vol. fraction				
	Before drying						After drying		
	LCO	AB	PVdF	NMP	LCO	AB	LCO	AB	PVdF
Cathode slurry	100	4	6.5	75	19.5	2.0	78	8	14
AB slurry		4	6.5	75	-	2.5	-	36	64
LCO slurry	100		6.5	75	19.9	-	84	-	16

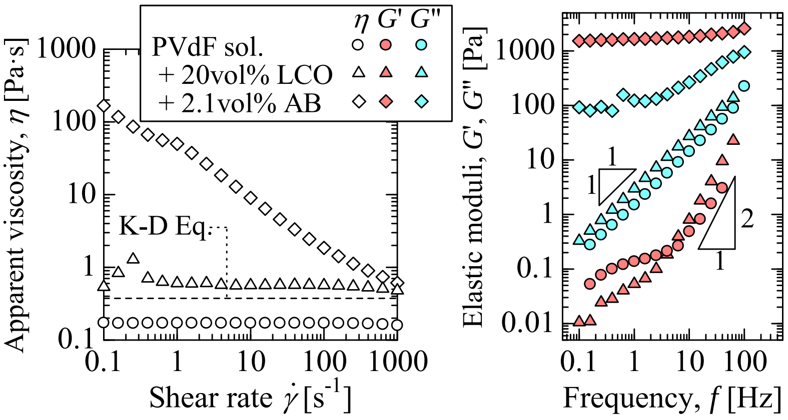
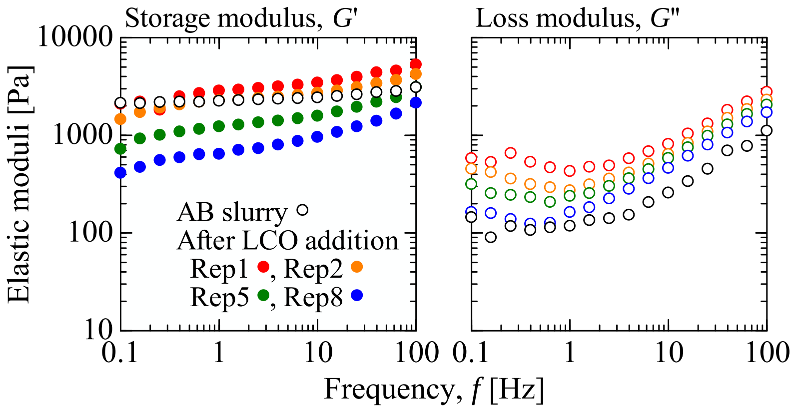


Fig.2 Rheological properties of AB and LCO slurries, and PVdF solution

It is found that the apparent viscosities of PVdF solution and LCO slurry were constant. The constant viscosity of LCO slurry was reasonably predicted by Krieger-Dougherty equation [8] and the Newtonian viscosity of 8wt% PVdF solution, shown as dotted line, implies that LCO particles were almost in the status of complete dispersion. In the viscoelastic characterization of these materials, viscous term or loss modulus *G''* of LCO slurry was slightly larger than that of PVdF solution similar to viscosity, whereas elastic term or storage moduli *G'* were almost same between PVdF solution and LCO slurry and were much smaller than *G''*. Those facts support that PVdF solution dominates the rheological behavior of LCO slurry and LCO particles are sufficiently separated each other having no noticeable interaction. On the other hand, AB slurry showed remarkable shear-thinning behavior in apparent viscosity. Additionally, storage modulus was significantly large and roughly constant regardless of frequency, and loss modulus was much smaller than *G''* and took constant value only at low frequencies were observed. Therefore, AB particles aggregated each other in PVdF solution and then formed high-ordered bridging structure. The following conclusion can be drawn in this section: the rheological behavior of cathode slurry was mainly affected by the degree of networking of AB particles and the status of the aggregated structure of AB particle must be changed depending on slurry preparation process.


Storage modulus, *G'*

Loss modulus, *G''*

Fig.3 Viscoelastic property change of AB slurry with the addition of LCO particles and with the repetition of dispersion

Full portion of LCO particles were added into the sufficiently dispersed AB slurry and the mixture was subjected to the repetition of dispersion. Although AB slurry showed no further change in rheological properties after 6times dispersion, the drastic rheological change was observed through the repetition of dispersion after the addition of LCO particles into AB slurry. The viscoelastic properties after each dispersion was measured as shown in Fig.3. In the comparison between AB slurry and the cathode slurry at the end of 1st dispersion (Rep.1), the increase of loss modulus *G''* can be roughly explained by the increase in viscous term with the addition of 20vol% of LCO particles, and the magnitude of G'' was gradually decreased and attained steady state after the 8th dispersion. Although lowering of *G''* means the progress of particle dispersion, *G''* always showed constant at low frequencies, which is called as "second plateau" and indicates the formation of bridging structure of particles, even after the 8th dispersion (Rep.8). Additionally, the magnitude of the storage modulus *G'* of cathode slurry after 1st dispersion was roughly same with AB slurry and was then significantly reduced with the progress of dispersion. Therefore, it was concluded that the bridging structure of aggregated AB particles still exists at the end of 2-step dispersion process, while the bridging structure could be broken up into smaller pieces under dispersion coexisting with larger LCO particles. The conclusion also suggests that LCO particles have a role like "ball media in a ball milling process" in the preparation process of cathode slurry to obtain more dispersed status of highly aggregated AB particles.

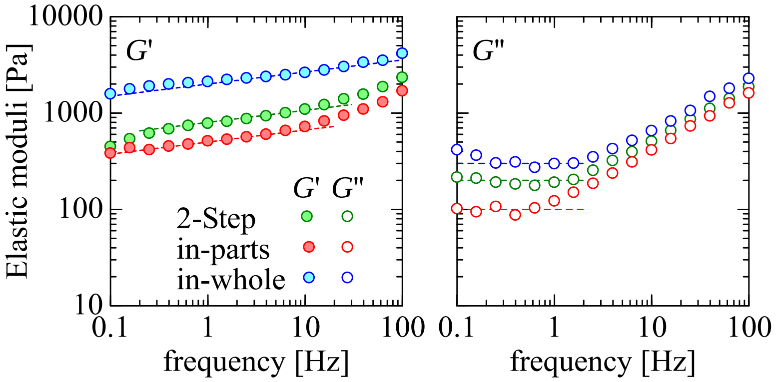


Fig.4 Comparison of viscoelastic properties of cathode slurries prepared by different methods

The viscoelastic property of 2-step slurry was compared with in-parts and in-whole slurries as shown in Fig.4. As common features of all slurries, the frequency dependency of *G'* was very small with the power of 0.15 and *G"* in the low frequency regime was roughly constant. These findings indicate that the bridging structure of AB particles were more or less formed in cathode slurry regardless of slurry preparation processes. However, the magnitude of *G'* for all frequency range and that of *G"* at the second plateau became larger in order of "in-parts", "2-step", and "in-whole". Larger elastic modulus corresponds to larger size of bridging structure of AB particles. Therefore, less aggregated state of AB particles is obtained in the in-parts slurry, and AB particles in the in-whole slurry was highly aggregated. The ball milling effect seems to be more significant in the in-parts dispersion process compared to 2-step process, since LCO and AB particle can coexist with smaller amount of NMP or in more viscous PVdF solution. Therefore, in-parts and in-whole slurries were used in the evaluation of film shrinking process.

Shrinkage behavior of the film of cathode slurry under drying conditions

Before showing the shrinking process of coated slurries, the typical result and its non-dimensional analysis are briefly described. An example of film thickness change was shown in the left figure of Fig.5. The film thickness was decreased linearly with time in the initial stage. At the very beginning of this stage, nonlinear film shrinking was sometimes observed due to the leveling of coated film under slow drying process or due to gradual increase of drying rate in a pre-heating regime under quick drying condition. In the former case, therefore, the film thickness change was obtained so that the extrapolated value of liner decreasing period coincides with the initial film thickness calculated from initial coated weigh. During the liner decreasing period, LCO and AB particles coexisted in a concentrated PVdF solution and the shrinking rate was determined by the evaporation rate of solvent from PVdF solution. On the contrary, when drying at high temperature, it takes long time for the film to be heated and the evaporation rate is thus increased gradually. This is the second mechanism of nonlinear film shrinking process. After the linear decreasing period, the decreasing slope became smaller and the thickness finally attained constant value. The volume fraction of PVdF was much smaller than that of void between particulate materials, so the coated film finally became porous at the end of the film shrinking process.

In spite of fixed conditions of slurry coating and drying, the initial film thickness and drying rate were slightly scattered among experimental runs. Additionally, the shrinking behavior at different drying condition cannot be directly compared because of large difference in the drying time. Therefore, the thickness and time were respectively non-dimensionalized by the following manners. Thickness was normalized by its initial value, which expresses the shrinking ratio of the coated slurry and converted into the void fraction in the drying film using the initial solid volume fraction. In contrast, time was divided by the newly introduced "evaporation time", which is the time required to completely evaporate the solvent at the drying rate in the linear decreasing period. The normalized time with the evaporation time is an index to show the degree of solvent remained in the drying film.

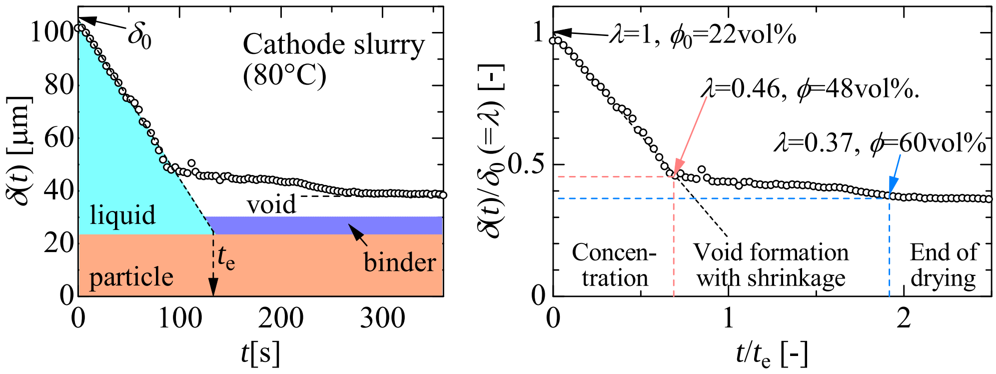
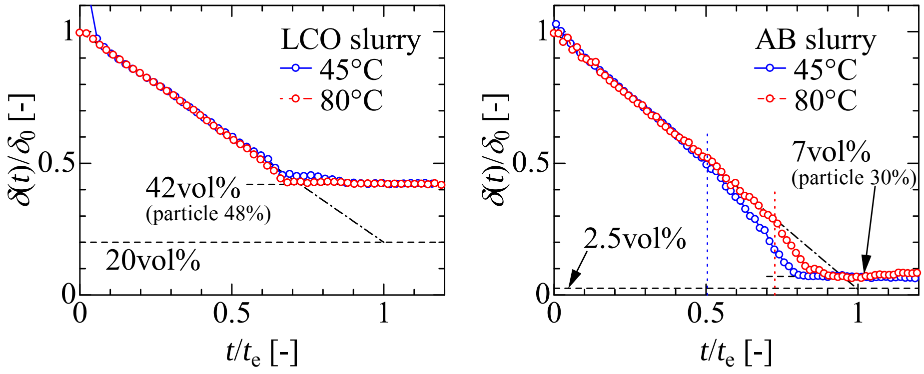


Fig.5. Typical results of film shrinking process and dimensionless analysis

As basic knowledge to understand the shrinking behavior of coated cathode slurry, the drying process of the coated films of AB and LCO slurries was firstly studied according to the similar manner to rheological characterization. The normalized shrinking behavior of those slurries at the heater temperature of 45 and 80°C are shown in Fig.6. The shrinking rate was 4 or 30 μm/min at each drying condition and was not changed between AB and LCO slurries. It is totally obvious because the shrinking rate in the linear decreasing period corresponded to the evaporation rate of solvent, which solely depends on drying temperature in the current study.

In the case of LCO slurry, the thickness was linearly decreased all the way until showing constant value without showing gradual decrease in shrinking rate. The particle volume fraction at the terminated thickness was calculated as 48vol% from the final shrinking ratio of 42% and the initial particle volume fraction of 20vol%. No difference in dimensionless shrinking behavior with drying temperatures was observed. Rheological characterization indicated that LCO particles were sufficiently separated each other in the PVdF solution. LCO particles, therefore, individually settled down and formed laden packing layer due to large size and specific density. In order to make sufficiently large void space for the evaporation of solvent, it is supposed that LCO particles formed more porous particle layer than random loose packing, which is reported to have the packing fraction of 55vol% [9].

On the other hand, in the case of AB slurry, the constant shrinking rate was observed until roughly half portion of solvent was evaporated (t/t_e < 0.5-0.7). After that, it is curious that the shrinking rate or decreasing slope was temporally increased for both drying temperatures. That is, the film shrinking rate became larger than the aforementioned evaporation rate. In this stage, the drying front was actually about to pass through the thickness measuring point. Therefore, the lateral evaporation of solvent contributes to the further large shrinking rate. This figure clearly showed that the effect of lateral drying on the film shrinking process was more significant for slower drying condition. Additionally, the final shrinking ratio was roughly 7vol%, which corresponds to 30vol% of particle volume fraction in the dried film. Considering the composition of AB slurry as shown in Table 1, the volume ratio of AB and PVdF was approximately 36:64 in the dried film. Therefore, it is expected that most AB particles were immersed in the dried PVdF film.



Shrinking rate

[ºC]	LCO	AB
45	3.9	3.7
80	32	32

[μm/min]

Fig.6 Dimensionless shrinking process of the films of LCO slurry and AB slurry

In the final section, the shrinking behavior of cathode slurry drying at the heater temperature of 45, 80, and 100ºC were studied and the results of in-parts and in-whole slurries were shown in Fig.7. According to the composition of cathode slurry, even if LCO particles form random loose packing layer with the packing fraction of 55vol%, it is considered based on simple calculation that the void space (45vol% of film) was partially filled with AB particles(6%) and PVdF (10%). Therefore, a coated cathode slurry finally turned into porous film and the void space between LCO particles will not be completely filled with AB or dried PVdF. It is found for the shrinking process of cathode slurry that the packing accompanied by void formation of LCO particles and AB particles is simultaneously taken place during drying.

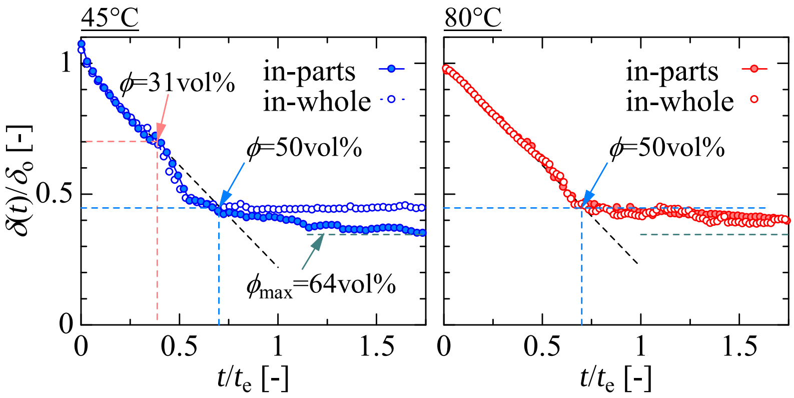


Fig.7 Effect of the aggregated status of AB particles and drying temperature on film shrinking behavior of coated cathode slurry

At the drying temperature of 45ºC, the film thickness was linearly decreased until 39% of solvent was evaporated, and then the decreasing rate became larger presumably due to the effect of lateral drying similar to AB slurry. Apparently, the effect of lateral drying on shrinking behavior became noticeable earlier compared to AB slurry. However, the volume ratio of NMP to AB was increased from 38 (before drying) to 18 at the end of linear decreasing period for AB slurry and cathode slurry. Therefore, the drying process of AB slurry was not affected by the existence of large LCO particles. After the drying front passes through the thickness measuring point, the thickness decreasing rate was drastically reduced. No difference in film shrinking process was not still observed between in-parts and in-whole slurries. However, when the dimensionless drying time exceeded 0.7 and the particle volume fraction became larger than 50vol%, the shrinking behavior was affected by slurry preparation process. At this point, the volume ratio of NMP to AB was further decreased to 3, where the PVdF solution was concentrated to 50wt%. As a feasible explanation, LCO and AB particles were bounded by wet PVdF swelled by NMP, and those particles can be slightly rearranged which enables to further increase packing density. However, it is assumed that the bridging structure of AB particles in in-whole slurry was large and may expand to cover LCO particle, and the rearrangement of LCO particles or further film shrinkage was not taken place. In contrast, cathode film from in-parts slurry attained random maximum packing of 64vo%. This is probably because the rearrangement of LCO particles is acceptable in-parts slurry containing smaller size of AB aggregates.

As seen in the shrinking behavior at the drying temperatures of 80 and 100ºC, the thickness decreasing trend was scarcely affected by slurry preparation process. A temporal increase in thickness decreasing rate was not observed similar to AB slurry dried at 80ºC. Therefore, inhomogeneous drying process in lateral direction of cathode slurry is originate in the drying characteristics of AB slurry coated film. Two obvious differences in the shrinking process with drying temperatures were observed. The first one is non-linear shrinking process only at the drying temperature of 100ºC. As already described, it takes longer time for the coated film to heat up to higher drying temperature and the evaporation time was much shorter than others. Therefore, the gradual increase of thickness decreasing rate in the pre-heating regime was not negligible in the shrinking behavior. The second one is the particle volume fraction at the end of the initial linear decreasing period. The content of particulate materials was increase up to 50vol% at 45 and 80ºC, but reached plateau of 40vol% at 100ºC. This is probably because LCO particles were loosely packed due to very large evaporation of solvent. The terminal velocity of LCO particles in 8wt% PVdF solution at room temperature was calculated as 36 μm/min, which is much smaller than the thickness decreasing rate of 100μm/min at 100ºC.

Conclusion

The mechanism of dispersion process of LCO and AB particles in PVdF solution was studied from rheological point of view in order to understand the effect of slurry preparation process on the internal structure of cathode slurry. It is found that the broken-up of strong bridging structure of AB particles is crucial for obtaining preferable cathode slurry and the dispersion of AB particles with LCO particles with smaller amount of solvent is suitable for the purpose.

The shrinking behavior of LCO and AB slurry was firstly investigated. It was found that heavy LCO particle formed random loose packing layer as long as shrinking rate is comparable to terminal settling velocity. In contrast, the effect of lateral drying was significantly observed for AB slurry at slow drying condition, and AB particles were finally immersed in the dried PVdF. At sufficiently slow drying condition, the drying of AB slurry and the formation of loose packing of LCO particles were simultaneously occurred. At this condition, swelled PVdF and smaller size of AB aggregated structure enables to rearrange LCO particles to obtain maximum random packing state. As increasing drying temperature, the final packing state was dominated by the packing behavior of LCO particles. The slower the film shrinking rate is, the more LCO particles are tightly packed.

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