Parametric study of dry coating process of electrode particle with model material of sulfide solid electrolytes for all-solid-state battery

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Abstract

We have reported that a dry coating is a very promising process to produce a suitable composite particle for all-solid-state lithium-ion secondary batteries. We here present a parametric study of this dry coating process for further optimization and improvement. In the dry coating process, electrode particles were coated with solid electrolyte (SE) particles. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) was used as a host particle, while sodium sulfate (Na_2SO_4) was selected as a model material of sulfide SEs and used as a guest particle. A dry impact-blending process known as “Hybridizer” was used. Effects of critical process parameters including tip speed of rotor, processing time, and initial weight fraction of host and guest particles were investigated. Under insufficient impact force NCM particles were not fully covered with Na_2SO_4 particles, while under a sufficient impact force the discrete coating of Na_2SO_4 particles on the surface of NCM particles were observed. With an increase in the mechanical input energy per unit mass of Na_2SO_4 , plastic deformation and coalescence of Na_2SO_4 particles were promoted, resulting in the continuous coating. With further increase in the mechanical input energy, breakage of the NCM particles was caused. The continuous coating exhibited a great advantage over the discrete coating for formation of [the solid-solid interfacial contacts](#) between NCM and Na_2SO_4 in the compressed pellet. Finally, the optimal processing conditions, where NCM particles are able to be coated by the continuous layer of much less amount of Na_2SO_4 (= 10 wt%) without breakage of NCM particles, were determined.

Keywords: dry coating; all-solid-state battery; composite particle

1. Introduction

A new next generation secondary battery for large-scale power storage devices has been strongly required for hybrid electric vehicles (HEVs) and electric vehicles (EVs), renewable energy productions, smart grid applications, and so on [1, 2]. Lithium-ion secondary batteries (LIBs), which are widely used in portable electronic devices, are considered as a potential candidate for the large-scale secondary battery. However, LIBs have a serious safety concern for application to the large-scale battery, because the organic liquid electrolytes used in the current LIBs are flammable. As a promising candidate of next generation secondary battery, all-solid-state lithium-ion secondary batteries (ASS-LIBs) have attracted much attention [3-5]. In the ASS-LIBs, inorganic solid electrolytes (SEs) are used instead of the organic liquid electrolytes. SEs are non-flammable materials and stable under higher voltage and broad temperature range. Due to these features, the ASS-LIBs are highly expected to be a next generation secondary battery with both high safety and high energy density.

For development of the ASS-LIBs, there are two major issues: (1) synthesis of new inorganic materials for SEs, and (2) development of processing technologies to produce composite electrodes. The lithium-ion conductivity of typical SEs was lower than that of organic liquid electrolytes [4]. To date, material scientists have synthesized new inorganic materials with higher lithium-ion conductivity. Among the candidate materials, sulfide SEs have been extensively investigated for the ASS-LIBs [3, 4, 6-10]. Recently, new sulfide SE which exhibits equivalent lithium-ion conductivity to organic liquid electrolytes has been synthesized [10]. However, high performance of the ASS-LIBs cannot be accomplished only by synthesizing new materials for SEs. In the ASS-LIBs, transfer of lithium ions during charging and discharging only occurs at the interfacial contact surface between an electrode particle and SE. This requires well-designed composite particles and electrodes in which solid-solid interfacial contacts between electrode particles and SEs for the lithium-ion conduction pathway is formed [3, 4]. Moreover, breakage of the electrode particles, that can lead to negative impact on the battery performance of the ASS-LIBs, should be avoided. Therefore, development of processing technologies to construct the solid-solid interfacial contacts in the composite particles and electrodes without breakage of the electrode particles is also important issue.

Many studies on the processing technologies to produce the ideal composite particles and electrodes have been reported. Some simple powder mixing techniques such as the use of smaller size of SEs [11] and wet mixing of electrode particles and SE particles [12] have been studied. These studies indicate that performance of the ASS-LIBs can be improved even by these simple powder handling

techniques. A planetary ball milling [13, 14] has often been used for mixing of electrode particles and SE particles. To achieve better composite particles, agglomerates of fine electrode and SE particles should be disintegrated sufficiently without breakage of the electrode particles. However, no one has succeeded in such an ideal mixing, suggesting that the planetary ball milling is less suitable for the processing technology to produce the composite particles and electrodes. To produce better composite particles and electrodes, it is ideal that the primary electrode particles are individually coated with SEs without breakage of the electrode particles. Such an ideal coating has been examined by means of a pulsed laser deposition (PLD) [15, 16]. In this technology, SE layer can be deposited on surface of the electrode particles, resulting in coating of primary electrode particles with the SE. The authors demonstrated a significant improvement in the battery performance using the coated particles. However, the PLD has disadvantages of low throughput and much expensive running cost due to significant low formation rate of the coating layer. Thus, the PLD is very expensive and far from practical use in an industrial process [4]. Apart from the powder handling equipment, hot pressing at temperatures above the glass transition temperatures of SEs [17] have also been attempted. However, the heating treatment can reduce the battery performance.

In our previous study [18], we proposed to apply a dry coating process and reported that individual primary electrode particles (host particles) are able to be successfully coated with a model material of sulfide SEs (guest particles). In a compacted pellet (i.e., mimic of composite electrode) prepared from the coated particles, the solid-solid interfacial contacts between electrode particles and the model material of SEs are well formed, suggesting that the dry coating process is very effective to produce composite particles and electrodes with the ideal structure for the ASS-LIBs. However, effects of many processing conditions on the coated particles have not been investigated, and there is much room for further improvement and optimization of the process.

We here present a parametric study of the dry coating process. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) which is a typical cathode active material was used as a host particle. Sodium sulfate (Na_2SO_4) was selected as a model material of sulfide solid electrolytes and used as a guest particle. The dry impact-blending device was used as a dry coating device. Effects of critical process parameters including tip speed of rotor, processing time, and initial weight fraction of host and guest particles were systematically investigated. Through this investigation, mechanism of the dry coating in this study was discussed. Finally, the optimal processing conditions were determined.

2. Experimental

2.1. Equipment

A dry impact-blending process (Hybridizer NHS-0, Nara Machinery Co., Ltd.) was used as a dry coating device (Fig. 1). This device mainly consists of chamber (inside diameter of 125 mm, depth of 49 mm, and effective volume of $470 \times 10^3 \text{ mm}^3$), rotor with six blades (diameter of 118 mm), and circulation pipe. The dry coating was conducted as follows. A pre-mixed powder mixture of host and guest particles was fed into the chamber. The rotor was then rotated and the particles circulate in the device. During the circulation, the particles are subjected to high impact forces due to particle-to-wall and particle-to-particle collisions. As a result, agglomerates of the particles are disintegrated and surface of the host particles are covered with guest particles, resulting in the dry coating. After a predetermined processing time, the discharge valve is opened, and coated particles are collected.

2.2. Powder samples

$\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) (NCM-03, Toda Kogyo Corp.) and sodium sulfate (Na_2SO_4) (JIS special grade, Wako Pure Chemical Industries, Ltd.) were used as powder samples. Fig. 2 shows the volume based particle size distributions and SEM images of the powder samples. NCM is a typical positive-electrode active material for LIBs. Volume based median diameter of the NCM was 5.4 μm . NCM is relatively rigid, brittle, and electrically conductive material, as compared to Na_2SO_4 . NCM was used as a host particle in the dry coating. Na_2SO_4 was selected as a model material of sulfide SEs [18], because sufficient amount of sulfide SEs to conduct our experiments is commercially unavailable. For selecting a model material of sulfide SEs, we considered that following properties are important: (i) nature of the room-temperature pressure sintering; (ii) mechanical properties such as stiffness and elastoplasticity. It has been reported that sulfide SEs exhibit the unique densification property so called “room-temperature pressure sintering [16]”: when powder of a sulfide SE is compressed, the sulfide SE particles are able to be easily deformed and coalesced even at a room temperature. This results in a compressed pellet in which the original SE particles are continuously coalesced, and void spaces and particle boundaries are almost vanished. In this study, the model material of sulfide SEs was selected from a few inorganic materials which exhibit the room-temperature pressure sintering. We then measured the stiffness and elastoplasticity of the candidate materials by means of an indentation test [18]. As a result, Na_2SO_4 showed the room-temperature pressure sintering as well as similar stiffness and elastoplasticity with a sulfide SE [18]. Consequently, Na_2SO_4 was selected and used in this study as a model material of sulfide SEs. Na_2SO_4 is

relatively soft, ductile, and non-conductive material, as compared to NCM. Na_2SO_4 was used as a guest particle of the dry coating. The as-received powder of Na_2SO_4 was preliminarily milled by a multi-ring-type wet grinding system (MICROS-0, Nara Machinery Co., Ltd.). Volume based median diameter of the Na_2SO_4 after the wet milling was 0.95 μm .

2.3. Experimental procedure and conditions

NCM and Na_2SO_4 were pre-mixed by mortar-and-pestle mixing for 30 min. This pre-mixture was then processed by the dry impact-blending device. Table 1 shows processing conditions of the dry coating. Effects of the tip speed of rotor, processing time, and initial weight fraction of NCM and Na_2SO_4 particles were investigated. Total weight of NCM and Na_2SO_4 were 10.0 g in all experimental runs. The dry coating experiment was conducted one time at each Run. No., except for the Run No. 11. We confirmed that there is reproducibility in the dry coating experiment and there is no need to consider the batch deviation.

2.4. Characterization

FESEM equipped with an EDX spectroscopy (SU8200, Hitachi, Ltd.) was used to observe surface morphology of particles. A net weight fraction of NCM and Na_2SO_4 in the dry coated particles was measured by an ICP-AES (SPS7800, Seiko Instruments Inc.). To evaluate the breakage of NCM particles after the dry coating, Na_2SO_4 of the coated particles was washed out in water and size distribution of the NCM particles after the washing out was measured using a laser diffraction particle size analyzer (SALD-2100, Shimadzu Corp.). Compressed pellets, which mimic the composite electrode, were prepared from the dry coated particles. The coated particles of 0.50 g was initially charged into a die (10 mm of inner diameter) and compressed using a hand press at a compression pressure of 360 MPa. Inner wall of the die is made of non-conductive polyacetal resin, while the upper and lower punches were made of conductive stainless steel. A DC electrical resistivity of the pellet inside the die in vertical direction was measured using an electrometer (Model 6514, KEITHLEY). Increase in electrical resistivity normalized by the net weight fraction of Na_2SO_4 (R_{inc}) [18] was then calculated by:

$$R_{\text{inc}} = \frac{R_{\text{DC}} - R_{\text{NCM}}}{x_{\text{Na}_2\text{SO}_4}} \quad (1)$$

where R_{DC} and R_{NCM} are electrical resistivities of compressed pellets prepared from dry coated particles and prepared from NCM particles, respectively. $x_{Na_2SO_4}$ is the net weight fraction of Na_2SO_4 . States of the NCM- Na_2SO_4 interfacial contacts were evaluated using R_{inc} : if NCM is well coated with Na_2SO_4 and the NCM- Na_2SO_4 interfacial contacts are well formed, R_{inc} becomes higher due to non-conductivity of Na_2SO_4 ; if the NCM- Na_2SO_4 interfacial contacts are not well formed, networks of conductive NCM particles are formed in the pellet, thus resulting in lower R_{inc} . The NCM- Na_2SO_4 interfacial contacts in the pellets were also observed through FESEM observation of cross-section of the pellets. Cross-sections of the pellets were prepared using an argon ion beam cross-section polisher (IM4000, Hitachi, Ltd.).

3. Results and discussion

3.1. Effect of tip speed of rotor

Fig. 3a shows FESEM and EDX images of dry coated particles prepared at different tip speeds of rotor (Run No. 1, 2, and 3 in Table 1). Elemental mapping images of manganese and sulfur show the presence of NCM (host particle) and Na_2SO_4 (guest particle), respectively. At each tip speed, manganese of NCM and sulfur of Na_2SO_4 were detected at the same location, confirming that NCM particles were covered with Na_2SO_4 . At 50 m/s of tip speed, surface morphology of the pristine NCM (rectangular-shaped grains) was still observed, although NCM particles were partially covered with Na_2SO_4 particles. At 80 m/s, the surface morphology of the pristine NCM was no longer observed and NCM particles were almost fully covered with Na_2SO_4 . In our previous study, fundamental mechanism of this dry coating process was revealed [18]: soft guest particles (Na_2SO_4) are plastically deformed and coalesced with each other on a rigid host particle (NCM) due to high impact force derived from the dry impact-blending process. This results in formation of the coating layer of Na_2SO_4 . Thus, it was considered that 80 m/s of tip speed can provide sufficient impact force for plastic deformation and coalescence of Na_2SO_4 particles, while the impact force at 50 m/s of tip speed was insufficient for the deformation and coalescence of Na_2SO_4 particles. At 100 m/s, further densification and discrete coating of Na_2SO_4 particles due to much higher impact force were observed.

Net weight fraction of NCM and Na_2SO_4 after dry coating at different tip speeds was shown in Table 1 (Run No. 1, 2, and 3). The net weight fraction of Na_2SO_4 after dry coating was lower than the initial weight fraction (30 wt%) at every tip speed. This is due to adhesion of Na_2SO_4 particles onto the inner wall of the chamber and circulation pipe of the dry impact-blending device. At 50 m/s of tip speed, the net weight fraction of Na_2SO_4 was significantly lower than the other higher tip speeds. This may be

due to less sticking of Na_2SO_4 particles onto NCM particles under too lower impact force.

Fig. 3b shows increase in electrical resistivity (R_{inc}) defined by the Eq. (1) as a function of tip speed of rotor. The coated particles prepared at 80 and 100 m/s showed remarkably higher R_{inc} than those prepared at 50 m/s. When the solid-solid interfacial contacts between conductive NCM particles and non-conductive Na_2SO_4 particles are well formed in the pellet, R_{inc} shows higher value. Thus, it was confirmed that the NCM particles were coated with Na_2SO_4 at 80 and 100 m/s of the tip speed, while the NCM particles were not well coated at 50 m/s of the tip speed. Fig. 3c shows size distributions of NCM particles after washing out Na_2SO_4 from the coated particles prepared at different tip speeds. Although a slight decrease in the particle size was found at the higher tip speed, change in the particle size distribution was subtle and not significant. Thus, NCM particles were not damaged at less than 100 m/s of the tip speed within 300 s of the processing time.

In summary, we found that the tip speed higher than 80 m/s can provide sufficient impact force for plastic deformation and coalescence of Na_2SO_4 particles, resulting in coated particles fully covered with the Na_2SO_4 particles.

3.2. Effect of processing time

Fig. 4a shows FESEM and EDX images of coated particles at various processing times (Run No. 4, 6, and 7 in Table 2). Both of manganese and sulfur were detected from same particle at each processing time. This indicates that NCM particles were covered with Na_2SO_4 . With an increase in the processing time, surface morphology of coated particles exhibited a significant change from the discrete coating (60 s and 600 s) to the continuous coating (1800 s). This is due to much higher mechanical input energy at longer processing time, promoting plastic deformation and coalescence of Na_2SO_4 particles.

Table 1 (Run No. 3 to 7) shows the net weight fraction of NCM and Na_2SO_4 after the dry coating at different processing times. The net weight fraction of Na_2SO_4 was almost constant at 20 wt% regardless of the processing time. This indicates that amount of Na_2SO_4 adhered onto the inner wall of the chamber and circulation pipe immediately reached to an equilibrium within 60 s. It is also considered that amount of Na_2SO_4 adhered onto NCM particles also reached to an equilibrium within 60s, followed by densification, plastic deformation, and coalescence of Na_2SO_4 with an increase in the processing time.

Fig. 4b shows increase in electrical resistivity (R_{inc}) as a function of the processing time. It should be noted that coated particles prepared at 1800 s of the processing time showed remarkably higher R_{inc} . This means that the continuous coating (Fig. 4a at 1800 s), that is more stable than the discrete

coating, can provide a more ideal structure in the compressed pellet: the solid-solid interfacial contacts between conductive NCM and non-conductive Na_2SO_4 can be well formed from coated particles covered with the continuous coating layer. Fig. 4c shows particle size distributions of NCM particles after washing out Na_2SO_4 from the coated particles. Within 600 s of the processing time reduction in the particle size from that of the original NCM particles was not significant, suggesting that breakage of the host particles did not occur at an early stage of the dry coating. This is due to the cushioning effect of the guest particles. At much longer processing time (1800 s), however, significant decrease in the particle size due to breakage of the NCM was found. This may be due to an increase in the impact force acting on the NCM particles, resulting from thinning of the coating layer at longer processing time. Moreover, this may be due to the fatigue breakage of NCM particles at longer processing time.

In summary, a longer processing time, i.e., higher mechanical input energy, leads to formation of the continuous coating layer of Na_2SO_4 particles, although a longer processing time can result in significant damage of the NCM particles. It was also revealed that the continuous coating is desirable surface morphology for formation of a more ideal structure in the compressed pellet.

3.3. Effect of initial weight fraction of host and guest particles

For composite electrodes of the ASS-LIBs, higher content of electrode particles and lower content of SEs are desired to achieve higher energy density [4]. Thus, effect of the initial weight fraction was investigated within lower weight fraction of Na_2SO_4 than 30 wt% as shown in Table 1 (Run No. 8 to 10). Fig. 5a shows FESEM and EDX images of coated particles at different initial weight fraction of NCM and Na_2SO_4 particles. Detection of both elements (manganese and sulfur) from same single particle indicates that NCM particles were covered with Na_2SO_4 at each initial weight fraction. Even at relatively shorter processing time (= 300 s), the continuous coating was formed at less than 20 wt% of Na_2SO_4 , while the discrete coating was observed at 30 wt% of Na_2SO_4 (Fig. 3a at 100 m/s of tip speed). This is due to higher mechanical input energy per unit mass of Na_2SO_4 at lower fraction of Na_2SO_4 , promoting the plastic deformation and coalescence of Na_2SO_4 particles within shorter processing time.

Table 1 (Run No. 3, 8, 9 and 10) shows the net weight fraction of NCM and Na_2SO_4 after dry coating at different initial weight fraction. At initial weight fraction lower than 10 wt% of Na_2SO_4 (Run No. 9 and 10), the net weight fraction was almost unchanged from the initial weight fraction. This indicates that at the lower initial fraction most of the Na_2SO_4 particles were firmly adhered onto the NCM particles and turned to the continuous coating without loss of Na_2SO_4 due to adhesion onto the wall of the

dry coating device.

Fig. 5b shows increase in electrical resistivity (R_{inc}) as a function of the initial weight fraction of Na_2SO_4 . R_{inc} at 20 wt% of the initial weight fraction showed higher than that at 30 wt% despite lower net weight fraction of Na_2SO_4 . This confirms that the continuous coating is advantageous over the discrete coating for formation of the solid-solid interfacial contacts between NCM and Na_2SO_4 in the compressed pellet. At lower than 20 wt%, R_{inc} became smaller with a decrease in the initial weight fraction of Na_2SO_4 . This may be due to thinner thickness of the coating layer, inducing formation of electrical conduction pass of conductive NCM particles in the compressed pellet. Fig. 5c shows size distributions of NCM particles after washing out Na_2SO_4 from the coated particles prepared at different initial weight fraction of Na_2SO_4 . At less than 10 wt% of Na_2SO_4 significant breakage of NCM particles was observed due to less cushioning effect of Na_2SO_4 , while no significant breakage of NCM particles was observed at 20 and 30 wt% of Na_2SO_4 .

In summary, the continuous coating is able to be formed by decreasing the initial weight fraction of Na_2SO_4 particles, i.e., by increasing the mechanical input energy per unit mass of Na_2SO_4 particles. The initial weight fraction can be maintained after the dry coating at less than 10 wt% of the initial weight fraction of Na_2SO_4 .

3.4. Mechanism of dry coating in this study

Through the above-mentioned parametric investigations, mechanism of the dry coating process in this study was proposed as illustrated in Fig. 6. At an initial state (Fig. 6a), host particles (NCM) are partially covered with guest particles (Na_2SO_4) by the mortar-and-pestle pre-mixing. Under insufficient impact force, i.e., too low tip speed of rotor, host particles are not fully coated with guest particles but partially coated (Fig. 6b). Under excess impact force, it is expected that host particles can be immediately broken (Fig. 6g). Under a sufficient impact force, densification of guest particles on the surface of host particles occurs, resulting in the discrete coating (Fig. 6c). With an increase in the processing time, i.e., increase in the mechanical input energy, plastic deformation and coalescence of guest particles are promoted (Fig. 6d), resulting in the continuous coating (Fig. 6e). This morphological change is more pronounced at less initial weight fraction of guest particles due to higher mechanical input energy per unit mass of guest particles. With further increase in the mechanical input energy, breakage of the host particles is induced (Fig. 6f). It is considered that the dry coating mechanism shown in Fig. 6 can be applied to other type of powder handling equipment in which mechanical forces are imparted to the particles, while

the powder handling equipment which is able to achieve the continuous coating (Fig. 6 (e), suitable coating state for the ASS-LIBs) is considered to be limited.

3.5. Determination of optimal processing condition

Based on the above-mentioned mechanism, the optimal processing conditions were determined. To achieve better performance of the ASS-LIBs, following particle design is required in the dry coated particles: (1) no breakage of host (electrode) particles; (2) the continuous coating; (3) less fraction of guest (SE) particles. We proposed optimal processing conditions where the above-requirements can be fulfilled. The proposed optimal processing conditions were shown at Run No. 11 in Table 1. We preliminarily examined reduction in the initial weight fraction of guest particles and have found that the lower limit is 10 wt%. At less than 10 wt% of Na_2SO_4 , breakage of NCM was inevitable. To verify the proposed optimal conditions, the dry coated particles was prepared and characterized. Fig. 7a and b shows FESEM images of coated particles prepared at the proposed optimal conditions. NCM particles were fully covered with the continuous layer of Na_2SO_4 . Thickness of the coating layer was around 0.15 μm . The initial weight fraction of NCM and Na_2SO_4 was almost maintained even after the dry coating (Run No. 11 in Table 1). Fig. 7c shows size distributions of NCM particles after washing out Na_2SO_4 from the coated particles. No significant breakage of NCM was found even at relatively less fraction of guest particles. Fig. 7d shows FESEM images of NCM particle after washing out Na_2SO_4 from the coated particles. Surface morphology was unchanged from the pristine NCM (Fig. 2b). These results confirmed that NCM particles were able to be coated with less fraction of Na_2SO_4 (10 wt%) without breakage and attrition of the NCM particles. Fig. 7e and f shows FESEM images of cross-section of compressed pellet prepared from the coated particles. In the compressed pellet, NCM particles (light gray region) were well dispersed in Na_2SO_4 matrix (dark gray region) without agglomeration, and the solid-solid interfacial contact between electrode particles (NCM) and model material of SEs (Na_2SO_4) were well formed.

In this study, the guest particles with a bimodal particle size distribution were used. We consider that the bimodal size distribution of the guest particles would not affect the optimal processing conditions. One of the concerns raised by the bimodal size distribution is segregation of larger guest particles from host particles. This can result in significant variation of the net weight fraction of the host and guest particles after coating from the initial weight fraction. However, the result in this study showed that the initial weight fraction of host and guest was almost maintained (Run No 11 in Table 11). This means that NCM particles were coated with larger Na_2SO_4 particles as well as smaller Na_2SO_4 particles. Therefore, it

is considered that the bimodal size distribution of the guest particles used in this study would not affect the optimal conditions.

In most of the previous studies regarding the ASS-LIBs using sulfide SEs, weight fractions of SEs in the composite electrodes were higher than 30 wt% [4] to ensure ionic conducting pathways. Only Sakuda et al. [16] successfully reported coating of electrode particles with much less fraction of SE (= 10 wt%). However, they used a pulsed laser deposition (PLD) technique, which is costly and far from being a practical use in industrial sectors, while the dry coating process is much more practical. Thus, the dry coating process that can coat electrode particles with much less amount of SEs without damage of the electrode particles is very promising to produce composite particles and electrodes for the ASS-LIBs.

4. Conclusions

A parametric study of the dry coating process, in which electrode particles were coated with model material of sulfide solid electrolytes, was conducted. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) was used as a host particle. Sodium sulfate (Na_2SO_4) was selected as a model material of sulfide solid electrolytes and used as a guest particle. A dry impact-blending process known as “Hybridizer” was used. Effects of critical process parameters including tip speed of rotor, processing time, and initial weight fraction of host and guest particles were investigated.

Under too low tip speed of rotor NCM particles were not fully covered with Na_2SO_4 due to insufficient impact force, while under a sufficient tip speed NCM particles were fully covered and the discrete coating of Na_2SO_4 particles on the surface of NCM particles were observed. With an increase in the processing time, plastic deformation and coalescence of Na_2SO_4 particles were promoted, resulting in the continuous coating. This morphological change was more pronounced at less initial weight fraction of Na_2SO_4 due to higher mechanical input energy per unit mass of Na_2SO_4 . With further increase in the mechanical input energy, breakage of the NCM particles was caused. The continuous coating, that is more stable than the discrete coating, showed a great advantage over the discrete coating for formation of the NCM- Na_2SO_4 interfacial contacts in the compressed pellet. Based on the parametric investigations, the optimal processing conditions were finally determined. At the determined optimal conditions, NCM particles were successfully coated by the continuous layer of much less amount of Na_2SO_4 without breakage of NCM particles.

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Captions of Figures and Table

Fig. 1. Schematic of dry impact-blending device (Hybridizer).

Fig. 2. (a) Volume based particle size distributions of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM) and Na_2SO_4 . FESEM images of (b) NCM and (c) Na_2SO_4

Fig. 3. Effects of tip speed of rotor ([Run No. 1, 2 and 3](#)). (a) FESEM and EDX images of coated particles. (b) Increase in electrical resistivity as a function of tip speed of rotor. (c) Volume based size distributions of NCM particles after washing out Na_2SO_4 from coated particles.

Fig. 4. Effects of processing time ([Run No. 3, 4, 5, 6 and 7](#)). (a) FESEM and EDX images of coated particles. (b) Increase in electrical resistivity as a function of processing time. (c) Volume based particle size distributions of NCM particles after washing out Na_2SO_4 from coated particles.

Fig. 5. Effects of initial weight fraction of NCM and Na_2SO_4 ([Run No. 3, 8, 9 and 10](#)). (a) FESEM and EDX images of coated particles. (b) Increase in electrical resistivity as a function of initial weight fraction of Na_2SO_4 . (c) Volume based particle size distributions of NCM particles after washing out Na_2SO_4 from coated particles prepared at different initial weight fraction of Na_2SO_4 .

Fig. 6. Mechanism of dry coating in this study.

Fig. 7. Coated particles prepared at optimal processing conditions ([Run No. 11](#)). FESEM images of (a) coated particles and (b) cross-section of single coated particles. Light gray and dark gray region corresponds to NCM and Na_2SO_4 , respectively. (b) Volume based particle size distribution and (c) FESEM images of NCM particles after washing out Na_2SO_4 from coated particles. FESEM images of cross-section of compressed pellet prepared from coated particles at (e) lower magnification (x 2,000) and (b) higher magnification (x 5,000). Light gray and dark gray region corresponds to NCM and Na_2SO_4 , respectively.

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a

Tip speed of rotor = 50 m/s

Tip speed of rotor = 80 m/s

Tip speed of rotor = 100 m/s

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Table 1 Experimental conditions and net weight fraction of NCM and Na₂SO₄ after dry coating

Run No.	Tip speed of rotor [m/s]	Processing time [s]	Initial weight fraction of NCM : Na ₂ SO ₄ [wt%]	Net weight fraction of NCM : Na ₂ SO ₄ after dry coating [wt%]
1	50	300	70 : 30	87.3 : 12.7
2	80	300	70 : 30	78.5 : 21.5
3	100	300	70 : 30	79.8 : 20.2
4	100	60	70 : 30	78.9 : 21.1
5	100	180	70 : 30	76.3 : 23.7
6	100	600	70 : 30	79.1 : 20.9
7	100	1800	70 : 30	80.5 : 19.5
8	100	300	80 : 20	84.5 : 15.5
9	100	300	90 : 10	90.8 : 9.2
10	100	300	95 : 5	95.2 : 4.8
11	80	300	90 : 10	90.2 ± 0.5 : 9.8 ± 0.5*

*Average ± SD, *n* = 3

Initial weight fraction of guest particles