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Electrostatic Spray Deposition for Fabrication of Li-ion Batteries[†]

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Abstract

A dry powder deposition technique, namely electrostatic spray deposition (ESD), has been investigated for cathode fabrication of Li-ion battery. The specific features focused in this study were to prepare core/shell composite particles and examine their applicability for ESD. LiCoO₂ (LCO) was chosen as a cathode active material. Around the LCO particle, carbon nanoparticles as conductive additive were coated, followed by PMMA nanoparticles as binder additive, producing core/shell composite particles. The nanoparticle-coated unevenness on the LCO was capable of significantly improving the fluidity of the cohesive LCO particles. The composite particles also showed a good electrostatic charging ability. In addition, the PMMA nanoparticles in the outermost layer of the composite particles played a crucial role on a stable electrostatic deposition. Thus, LCO-based cathode film was successfully fabricated by ESD using the composite particles.

KEY WORDS: (Electrostatic Spray Deposition), (Composite particles), (Li-ion battery)

1. Introduction

Li-ion batteries are going to be more and more important for portable electronic devices. In addition, there is an increasing market share for storage batteries for environmentally friendly electric vehicles to reduce carbon dioxide emissions¹⁾.

In manufacturing Li-ion batteries, wet coating method is widely used. Slurries or pastes are prepared by mixing active particulate materials, binders, solvents and additives, and are fed to coating machines to be spread on current collector metals. Usually, organic solvents involving *N*-methylpyrrolidone (NMP) are used. However, these solvents contaminate air, land and water, because they are difficult to contain and recycle²⁾. It is therefore important to focus on reducing or eliminating solvent use through the development of solvent-free processes.

Electrostatic spray deposition (ESD) has been known to be a solvent-free process³⁾. ESD process involves charging particles as they pass through a “charging gun”; they then travel towards the metal surfaces grounded under the influence of aerodynamic and electrostatic forces. ESD has been applied for polymeric large particles (> 10 μ m in size) with an excellent fluidity, and it offers the benefits of depositing on large surfaces, high deposition rate, and of being easily scaled up⁴⁾.

On the other hand, the size of particles used in Li-ion batteries such as LiCoO₂, is at least an order of magnitude smaller. In this case, interparticle (or surface) forces arising mainly from van der Waals attraction are dominant enough to be strongly cohesive and poor fluidity. To our knowledge, ESD has not been utilized for manufacturing Li-ion battery.

Recently, we have investigated the design of fine particles to facilitate ESD for Li-ion battery⁵⁾. A typical cathode material, LiCoO₂ (LCO), was chosen as a model fine particle. It was found that the core/shell composite particles, in which shell nanoparticles (conductive/binder) were coated so as to surround the LCO core particle, can be applied to ESD. It was because the composite particles had a good fluidity as well as a good charging ability. Herein, we report the effects of the nanoparticle coating on ESD of LCO in detail, and also show the cathode performance of the resultant film.

2. Experimental procedure

Materials

LiCoO₂ (LCO) particles of diameter ~2 μ m in size were purchased from Nippon Chemical Industrial Co. Ltd. (Japan). Carbon black particles with ~40nm (Tokai Carbon Co. Ltd, Japan) were used as a conductive additive. PMMA particles of diameter ~100nm (Soken Kagaku Co. Ltd, Japan) were used as binder additive.

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Composite Particles

First, LCO and carbon particles were mechanically treated to prepare the carbon-coated LCO particles using the attrition type apparatus (Mechanofusion, Hosokawa Micron Corp.). Then, PMMA particles were coated in the same way, producing the composite particles of LCO/carbon/PMMA. The amount of added carbon and PMMA were 5mass% and 2mass%, respectively. Alumina nanoparticles of 0.2 mass% (Alu C, Nippon AEROSIL Co., Japan) were also mixed.

Electrostatic Spray Deposition

ESD can be classified into two types, corona-charging and tribo-charging. A corona-charging type has the disadvantages of Faraday cage effect and back-ionization⁹⁾, which deteriorate the coating layer performance. On the other hand, a tribocharging type does not have these disadvantages. Therefore, in this study, a tribo-charging system was used for the ESD experiment. The tribo-charging gun is made of polytetrafluoroethylene (PTFE), which produces positively charged particle in most cases. The positively charged particles are deposited on the grounded metal substrate. Our tribo-charging system is illustrated in **Figure 1**. The two PTFE guns (T-3a, Asahi Sunac Co. Japan) were placed facing each other. The distance between the two guns was of 500mm. The composite particles were fed to the two guns with feeding rate of 70g/min. The composite particles were charged in the gun with pressure of 0.2MPa, and sprayed into air (25°C, RH50%). The two emergent powder sprays met each at the center between the guns, producing the charged powder cloud. The grounded substrate (aluminum foil 150×150mm²) passed with a speed of 0.7m/min below the charged powder cloud. Since the Al substrate was positioned at a lower height than that of the two guns, the particles were not directly sprayed onto the substrate, but the particles were transferred onto the surface of the substrate by the electrostatic force. The deposited film was then roll-pressed, and disks of 16mm in diameter were stamped out for fabricating a half cell with a counter electrode of Li foil.

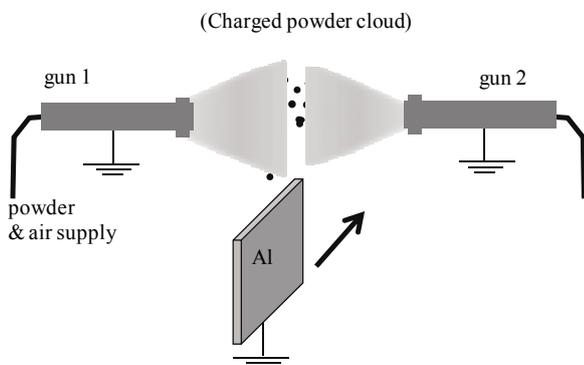


Fig. 1 Schematic illustration of our experimental apparatus.

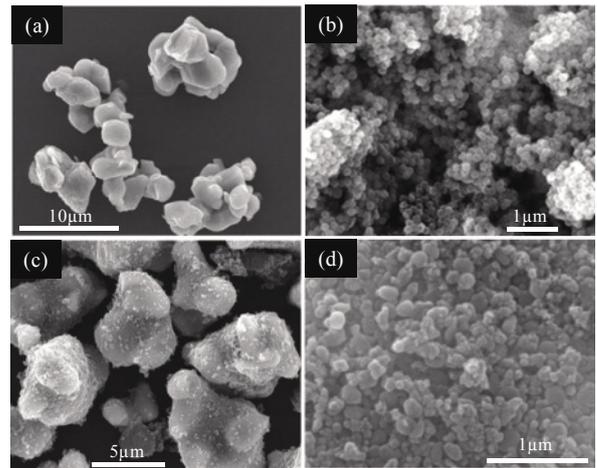


Fig.2 Representative SEM images of (a) LiCoO₂, (b) PMMA, (c) the composite particles, and (d) surface structure of the composite particles.

Characterization

The fluidity of the particles was determined from measurement of the angle of repose⁷⁾ (Powder tester, Hosokawa Micron Corp.). The charge to mass ratio of the composite particles was measured using a suction type of Faraday cage. Film density was calculated from the volume and weight of the film. Microstructural analysis of the composite particles and the films was performed using a scanning electron microscope (S-4100, Hitach High-Technologies Ltd.). Charge–discharge curve of the half-cell was obtained under charging at 0.1C in CC-CV mode, and discharging at 0.1C (SD-8, Hokutodenko Ltd.). Specific capacity was calculated based on the mass of active material in the electrode.

3. Results and Discussion

3.1 Properties of composite particles

The morphology and surface structure of LCO and LCO/carbon/PMMA composite particles were examined, as shown in **Figure 2**. As-received LCO particles had smooth surfaces and were bonded together to form irregularly secondary particles (Fig.2 (a)). Their mean particle diameter was determined to be about 7μm by laser diffraction and scattering method. The composite particles had uneven surfaces which were obtained by mechanical-coating of the carbon nanoparticles, followed by the PMMA nanoparticles (Fig.2(d)). Morphology and size of the composite particles were almost similar to those of LCO secondary particles, except for the surface structure (Fig.2(c)). In this study, the mechanical treatment was used for adhering and fixing the nanoparticles on the LCO surfaces rather than grinding the LCO secondary particles. Thereby, the core/shell composite particles were obtained, in which shell nanoparticles (carbon/PMMA) were coated around the core particles (LCO).

The LCO/carbon/PMMA composite particles had a good fluidity. The angle of repose has been known

to be quick test for monitoring the powder's flow and obtaining relative measures of fluidity. According to the literature ⁷⁾, angle of repose greater than 40° indicates a cohesive powder, while an angle greater than 50° indicates a very cohesive powder. In this study, the two-step coating (carbon and PMMA nanoparticles) was capable of significantly improving the fluidity of the cohesive LCO particles, with reducing its angle of repose from $\sim 70^\circ$ to $\sim 40^\circ$. The LCO/carbon composite particles had a good fluidity as well. The results indicate that the nanoscale unevenness on the LCO surfaces plays an important role for enhancing fluidity. It has been known that nanoscale surface roughness strongly reduces the van der Waals force between surfaces, and the reduction in the cohesion force is inversely proportional to the shell's nanoparticle size ⁶⁾. Furthermore, the hydrophobic coating layer of carbon and PMMA nanoparticles would be effective in improving the fluidity, due to the elimination of liquid bridges if any moisture is present ⁶⁾.

The LCO/carbon/PMMA composite particles had also a good charging ability. A suction-type Faraday Cage technique⁸⁾ was employed as a method for measuring the electrostatic charge of the composite particles dispersed into the air from the tribo-charging gun (PTFE). **Figure 3** shows the relationship between the accumulated charge of the composite particles collected in Faraday cage and the spray time. The observed linear relationship indicates that the composite particles was almost homogeneously charged and transferred to the Faraday cage with a constant velocity. The charge to mass ratio (specific charge) of the LCO/carbon/PMMA composite particles was estimated to be $\sim 3\mu\text{C/g}$ from measuring the accumulated charge and the mass of particles collected. That of LCO/carbon particles was of $\sim 2\mu\text{C/g}$. These values were comparable to those of polymer-based powders which are conventionally used for ESD⁹⁾. PTFE positions at lowest down in the tribo-electric series charges negatively¹⁰⁾, and consequently the particles under contact and collision with PTFE will be charged positively.

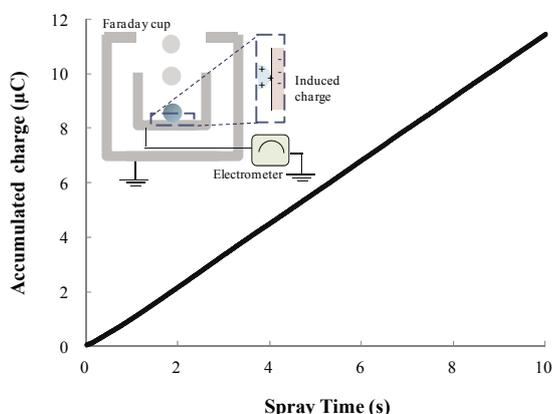


Fig. 3 Relationship between the accumulated charge and the spray time.

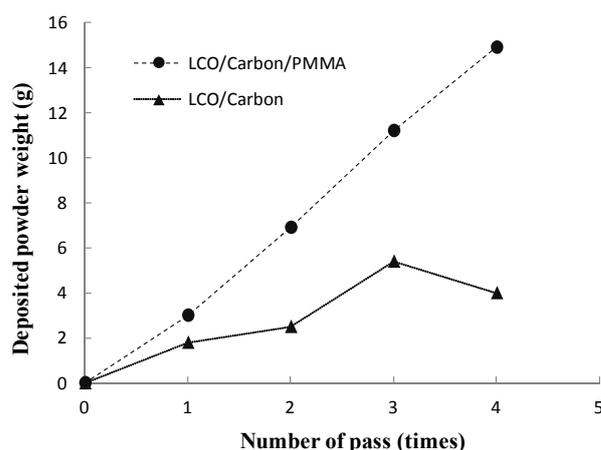


Fig. 4 Relationship between the deposited powder weight and the number of passing of Al foil.

3.2 Electrostatic dry coating

The LCO/carbon/PMMA composite particles were successfully coated on the Al substrate, while the Al substrate repeatedly passed below the charged powder cloud. As shown in **Figure 4**, the weight of the film increased almost linearly with increasing the number of passing (deposition rate $\sim 5\mu\text{m/s}$). The resulting film was flexible (**Figure 5(a)**) and had a relatively smooth surface on the whole of Al substrate (**Figure 5(b)**). The morphology, size and surface structure of the LCO/carbon/PMMA composite particles almost unchanged during deposition (**Figures 5 (c) (d)**). On the other hand, deposition behavior was unstable when using the LCO/carbon composite particles. It was observed the electrostatically deposited film was partly fallen off during deposition, indicating that electrostatic adhesion force between charged particles and Al substrate due to the creation of an image charge got lowered. Since LCO and carbon is conductive, rapid electrostatic discharging would occur after deposition and consequently lead to lowering the electrostatic adhesion force.

As can be seen, non-conductive PMMA nanoparticles (resistivity $>10^{14} \Omega\cdot\text{cm}$) in the outermost layer of the composite particles play a crucial role on stable ESD. In this study, the PMMA nanoparticles were added 2mass% against LCO/carbon composite particles. Their surface coverage was not 100%, but less than 50% in a rough estimation. Even their surface coverage, the discharging time prolonged, and the composite particles arrived at the substrate kept the electrostatic adhesion force during deposition. Further study is being progressed to address the relationship between surface resistance and discharging time constant in LCO/carbon/PMMA system.

3.3 Cathode performance

The film fabricated by the solvent-free ESD process, successfully worked as a cathode electrode of Li-ion battery. The apparent density of the as-deposited film containing was less than $2 \times 10^3 \text{kg/m}^3$. The film was then further pressed before assembling the half cell. The

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thickness of the pressed film was $\sim 70\mu\text{m}$, achieving the relatively high density ($3\times 10^3\text{kg/m}^3$). The pressed film was expected to be electrically connected to the LCO/carbon exposed non-PMMA coated surface. **Figure 6** shows the representative initial charge-discharge curves of LCO taken for the pressed film. The curves are very similar to those obtained for wet-coated films, and the specific capacity of the sample was measured to be about 140mAh/g , suggesting that the film would be applicable for cathode electrode.

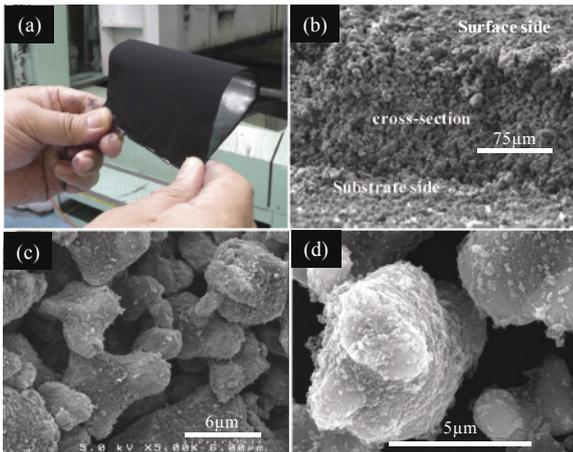


Fig. 5 (a) Deposited and cured film being bent in half. (b, c) cross-sectional SEM images of the deposited film after two passes. (d) LCO/carbon/PMMA composite particles sampled from the as-deposited film.

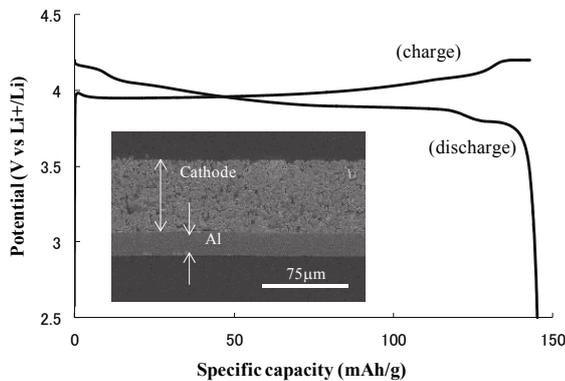


Fig. 6 Charge-discharge curves of LCO, taken for the pressed ESD film (inset: a cross-sectional SEM image of the pressed ESD film).

4. Summary

The commercial LCO particles were coated mechanically with carbon nanonparticles followed by PMMA nanoparticles. The resultant core/shell composite particles had a good fluidity. In addition, using tribo-charging gun, the composite particles were charged enough for ESD. Thus, LCO-based cathode film was successfully fabricated by the solvent-free powder processing (ESD). It is expected that there are some opportunities for the practical implementation of the present solvent-free processing for manufacturing not only Li-ion batteries but also functional composite films.

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