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Electrostatic Dry Coating of Cathode Materials for Li ion battery

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Organic solvents are widely used in wet coating for manufacturing Li ion batteries. This study focused on switching to environmentally benign solvent-free process, and examined a possibility of electrostatic dry coating (EDC) of cathode materials which are generally composed of active oxides, conductive and binder additives. Firstly, the composite particles containing the three components were prepared by dry mechanical treatment, and then EDC experiment was performed for the composite particles. Interestingly, the composite particles could be tribo-charged enough for electrostatic deposition on an earthed Al foil in air, with relatively high deposition rate. The as-deposited film was further dry-pressed to increase the film density (3×10^3kg/ m^3). A half cell was assembled using the pressed film as cathode electrode, and it was demonstrated that the initial charge-discharge characteristics were comparable to those obtained for wet-coated films. The results obtained indicate that there are some opportunities for the practical implementation of the EDC method for manufacturing functional composite films.

Keywords, Electrostatic dry coating, tribo-charge, composite particles, Li ion battery, cathode

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 emissions [1].

At present, wet coatings are applied to manufacture Li ion batteries. Pastes are prepared by mixing active particulate material, binders, solvents, and additives and are fed to coating machines to be spread on current collector foils, such as aluminum for the cathode side and copper for the anode side. NMP (*N*-methylpyrrolidone) is widely used. In general, however, organic solvents are difficult to contain and recycle completely [2]. It is therefore important to focus on reducing or eliminating solvent use through the development of solvent-free processes for fabricating Li ion batteries.

Electrostatic dry coating (EDC) may be a possible candidate as a solvent-free process, when depositing particulate materials onto metallic film or parts [3]. EDC process involves charging the particles as they pass through a "gun"; they then travel towards the earthed metal surfaces under the influence of aerodynamic and electrostatic forces. The EDC method has been well applied for polymer-based powders in paint industry [4, 5], and it offers the benefits of depositing on large surfaces, high deposition rate, and of being easily scaled up. If particulate materials for Li ion batteries are well charged, they can be deposited on current collector foils. However, much has never been explored for EDC using such active materials.

Here, we report an EDC method to deposit cathode composite materials which consisted of an active material ($LiCoO_2$), conducting additive (carbon black) and binder (PMMA). It was found that they were well charged using a "tribo-charging gun" which relies on frictional charging in a polytetrafluoroethylene (PTFE) tube, and they were successfully deposited on aluminum foils. In addition, the cathode prepared from the EDC-deposited film exhibited a good specific capacity.

2. Experimental Procedures

Materials

As a model cathode material, $LiCoO_2$ (LCO) with layered rocksalt structure (primary size ~2.5μm) was purchased from Nippon Chemical Industrial Co. Ltd. (Japan). A carbon black powder (~40nm, Tokai Carbon Co. Ltd, Japan) and a PMMA powder (~100nm, Soken Kagaku Co. Ltd, Japan) were used as conductive and binder additives. First, LCO and carbon powders were mechanically treated using an attrition type apparatus [6, 7] to prepare the carbon-coated LCO particles. Then, PMMA particles were coated in the same way, producing the composite particles of LCO/carbon/PMMA. The amount of added of carbon and PMMA were 5mass% and 2mass%, respectively. 0.2mass% of alumina nanoparticle (Alu C, Nippon AEROSIL Co., Japan) was also mixed as chargeable agent.

Electrostatic Dry Coating

In this study, a simple EDC system was set up using tribo-charging guns (T-3a, Asahi Sunac Co. Japan), as shown in Fig.1. The main part of guns is PTFE tube (internal diameter 6mm) in which powder materials can be charged. PTEF is often used material for tribo-charging. The two guns were placed facing each other. The distance between the two guns was 500mm. The composite particles were fed to the two guns with feeding rate of 70g/min. The composite powder was charged in the gun under applying the pressure of 0.2MPa, and spayed into air (25, RH50%). The two emergent powder sprays met each at the center between the guns, producing the charged powder cloud. The grounded substrate (aluminum foil 150×150mm^2) passed through with speed of 0.7m/s in the powder cloud. Since the substrate was positioned at lower height than that of the two guns, the particles were directly sprayed onto the substrate, but the particles in the powder cloud transferred onto the surface of the substrate by electrostatic force.

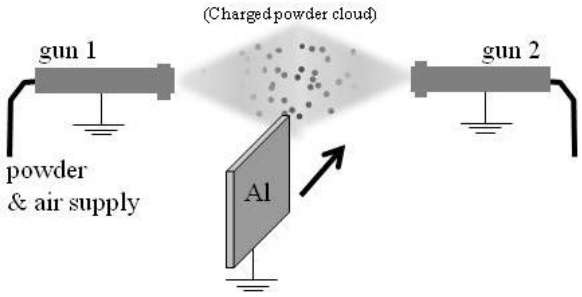

Fig.1 A schematic of our EDC system

The as-deposited film was then roll-pressed, and the disks with 16mm in diameter were stamped out for fabricating a half cell with a counter electrode of Li foil.

Characterization

The charge to mass ratio of the composite powder was measured using a suction type of Faraday cage [8,9]. Film density was calculated from volume and weight of the film. Microstructural analysis of the composite powder and the films was performed using a scanning electron microscope. Charge–discharge curve of the half-cell was obtained under charging at 0.1C in CC-CV mode, and discharging at 0.1C. Specific capacity was calculated based on the mass of active material in the electrode.

3. Results and Discussion

3.1 *Structure of composite particles*

Figure 2 (a) shows a representative SEM image of LCO particles. Several or more LCO particles are bonded together to form secondary particles. Their mean particle diameter determined by a laser diffraction and scattering method was about 7μm. Fig. 2(b) shows a SEM image of the composite particles. The carbon and PMMA particles are observed on the surfaces of LCO particles. The mean particle diameter of the composite particles was almost the same as that of LCO (see Fig.3). Obviously, the finer carbon/PMMA particles are adhered and fixed on the larger LCO secondary particles.

An attrition-type mechanical milling [7] was employed to form the composite particles without using of organic solvent or water dispersion, which is also favourable regarding environmental friendless. The formation of such pseudo-core/shell composites is advantageous in not only achieving a good mixing state of the three components but also improving powder fluidity. In general, particles smaller than 10μm have very poor fluidity due to the strong cohesion force arising mainly from Van der Waals attraction [10]. Fortunately, nanoparticle coating on such micron-sized particles can reduce the van der Waals forces between them and thereby fluidity can be improved [11]. The improved fluidity was very effective for stable feeding and tribo-charging of the composite particles for the present EDC experiments.

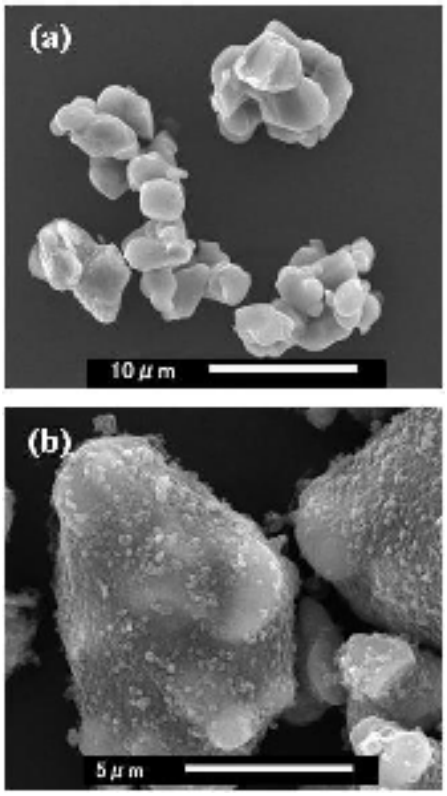

Fig.2. Representative SEM images of (a) LCO particles, (b) LCO/carbon/PMMA composite particles prepared by mechanical treatment

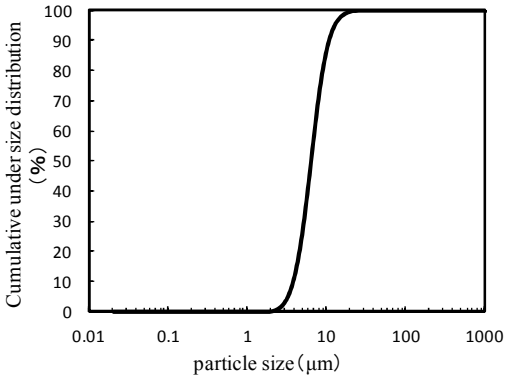

Fig.3 Size distribution of LCO/carbon/PMMA composite particles

3.2 *Electrostatic Charging of composite particles*

A suction-type Faraday Cage technique [8, 9] was employed as a method for measuring the electrostatic charge of the composite particles dispersed into the air from the tribo-charging gun. Figure 4 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 would be homogeneously charged and transferred to the Faraday cage with a constant velocity.

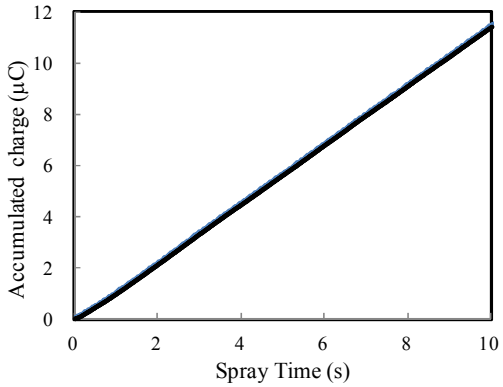

Fig.4 Relationship between accumulated charge of the composite particles and the spray time

The charge to mass ratio (or specific charge) of the composite particles was estimated to be about 3μC/g from measuring the accumulated charge and the mass of particles collected. This value is comparable to that of polymer-based powders which are conventionally used for EDC. Thus, it was found that the composite particles can be charged well using a tribo-charging gun.

The composite particles covering with mainly PMMA nanoparticles were positively charged (see Fig.4). The tribo-charging gun used was made of PTFE. It has been reported that PMMA can be positively charged when PTFE was used as charging material [12]. As well-known, PTFE positions at lowest down in the tribo-electric series charges negatively, and therefore the particles under contact and collision with PTFE would be charged positively. However, the charging mechanism of the composite particles has not been fully examined yet.

3.3 *Electrostatic dry Coating*

Since the composite particles can be easily charged and dispersed into air, we performed an EDC experiment, as illustrated in Fig.1. It was observed that the composite particles were deposited on the whole surface of the Al foil, as the Al foil passed through the charged powder cloud. As shown in Fig.5, the weight of the composite particles deposited on the Al foil increased almost linearly with the number of passing, indicating that the composite particles would be transferred onto the substrate with a constant velocity and deposited. The thickness of the film deposited after 1 pass was of ~70μm (see Fig.6).

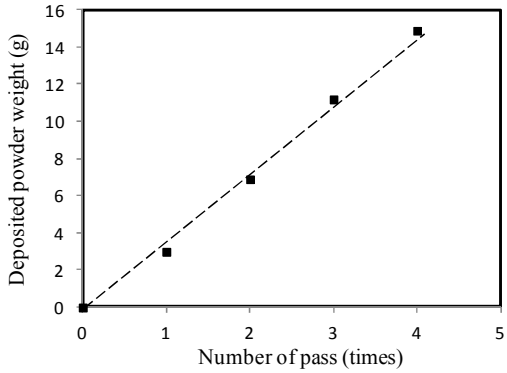

Fig.5 Relationship between the deposited powder weight and the number of pass of Al foil

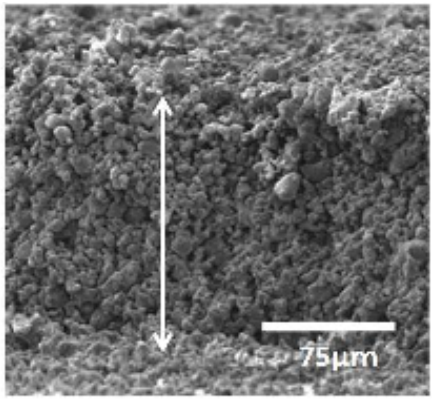

Fig.6. A cross-sectional SEM mage of the film deposited on Al foil (after two pass)

It is demonstrated that the charged composite particles can be dry-deposited on relatively large area by electrostatic forces. It also must be emphasized that relatively thick films can be obtained by this method. Although the mechanical properties of the film were not characterized, it had at least enough strength in assembly for a half coin cell.

3.4 *Cathode structure and performance*

The apparent density of the EDC film was less than 2×10^3kg/ m^3. The film was therefore further pressed before assembling the half cell to achieve the relatively high density (3×10^3kg/ m^3). Figure 7 shows cross-sectional SEM images of the pressed film. The magnified image (Fig.7 (b) revealed that the composite particles are densely packed in the pressed film. The thickness of the pressed film was ~70μm.

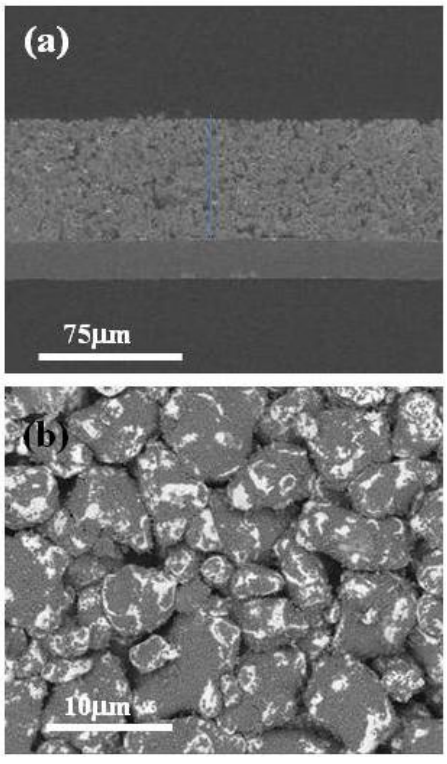

Fig.7 SEM mages of pressed film (a) low magnification, (b) higher magnification

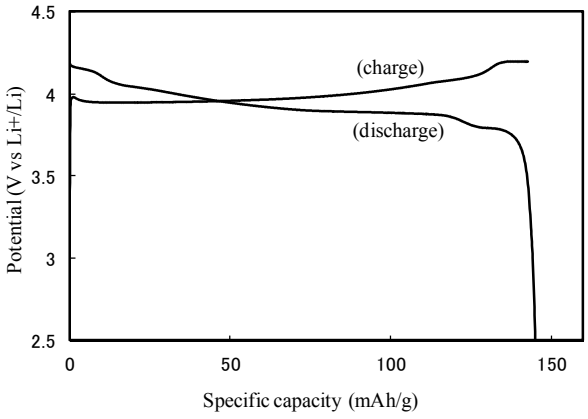

Fig.8 Charge-discharge curves of LCO, taken for the pressed EDC film

Figure 8 shows 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. These observations suggest that the film would be applicable for cathode electrode. The thick feature of the film would be also useful for increasing effective capacity.

To our knowledge, the thick cathode film was firstly prepared by the present all dry processing. It can be considered that morphological and microstructural design of the composite particles play important roles on not only EDC process but also performance of the resulting composite films. With this regard, a systematic study is being progressed, which will be reported in a near future.

4. Conclusions

We have investigated an electrostatic dry coating process as a solvent-free process for fabricating composite cathode layer of Li ion batteries. The important finding in this study was that the specific charge of the composite particles sprayed from tribo-charging gun had enough high for depositing them on earthed metallic substrate. We believe that there are some opportunities for the practical implementation of such solvent-free processing for manufacturing functional composite films.

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