

## Surface Treatment of LiFePO<sub>4</sub> Cathode Material for Lithium Secondary Battery

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**Abstract :** In this study, nano-crystallized Al<sub>2</sub>O<sub>3</sub> was coated on the surface of LiFePO<sub>4</sub> powders via a novel dry coating method. The influence of coated LiFePO<sub>4</sub> upon electrochemical behavior was discussed. Surface morphology characterization was achieved by transmission electron microscopy (TEM), clearly showing nano-crystallized Al<sub>2</sub>O<sub>3</sub> on LiFePO<sub>4</sub> surfaces. Furthermore, it revealed that the Al<sub>2</sub>O<sub>3</sub>-coated LiFePO<sub>4</sub> cathode exhibited a distinct surface morphology. It was also found that the Al<sub>2</sub>O<sub>3</sub> coating reduces capacity fading especially at high charge/discharge rates. Results from the cyclic voltammogram measurements (2.5-4.2 V) showed a significant decrease in both interfacial resistance and cathode polarization. This behavior implies that Al<sub>2</sub>O<sub>3</sub> can prevent structural change of LiFePO<sub>4</sub> or reaction with the electrolyte on cycling. In addition, the Al<sub>2</sub>O<sub>3</sub> coated LiFePO<sub>4</sub> compound showed highly improved area-specific impedance (ASI), an important measure of battery performance. From the correlation between these characteristics of bare and coated LiFePO<sub>4</sub>, the role of Al<sub>2</sub>O<sub>3</sub> coating played on the electrochemical performance of LiFePO<sub>4</sub> was probed.

**Keywords :** LiFePO<sub>4</sub>, Dry coating, Al<sub>2</sub>O<sub>3</sub>, Lithium ion battery

### 1. Introduction

Li-ion batteries, with high energy density and power capability, has become an important power source for portable electronic device, such as cellular phones and computers and, more recently, hybrid electric vehicle (HEV) and, electric vehicle (EV).<sup>1)</sup> Most commercialized Li-ion batteries use LiCoO<sub>2</sub> as a cathode material due to its ease of production, stable electrochemical cycling, and acceptable specific capacity.<sup>2,3)</sup> The relatively high cost of cobalt and the lure of large capacity have, however, lead to the study of other possible alternatives.

Among them, lithium iron phosphates have attracted particular interest, particularly LiFePO<sub>4</sub>, with a theoretical capacity of 170 mAhg<sup>-1</sup>.<sup>4)</sup> It is inexpensive, non-toxic and environmentally friendly. Unfortunately, the low intrinsic electronic conductivity of LiFePO<sub>4</sub> has been its main obstacle towards application in (H)EV. Many new approaches have been reported, including minimizing

LiFePO<sub>4</sub> particle size using various synthesis techniques, and forming conductive carbon coatings on the surface of LiFePO<sub>4</sub> particles through organic additives.<sup>5-8)</sup> Small particle size can facilitate the intercalation/deintercalation of lithium ions and enhance ionic conductivity. Conductive coating can raise the electronic conductivity. The combination of the two methods significantly increases rate capacity and cycle performance, but the carbon coating itself usually does not form a complete coating network on the LiFePO<sub>4</sub> particles due to a burning process [positive pressure of gas] of the organic material.<sup>9)</sup> During the intercalation process, the electrons cannot reach all the positions where Li<sup>+</sup> ion intercalation occurs, which results in electrode polarization. Therefore, enhancement of the rate capacity and cycle performance is usually limited. Fully complete coating with a conductive nano-layer ensures that LiFePO<sub>4</sub> particles receive electrons from all directions, consequently alleviating this polarization phenomenon.<sup>10)</sup> Thus far, there have been few reports on the conductive oxide coating on the LiFePO<sub>4</sub> particle surface because conventional coating method have difficult in

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preventing oxidation of  $\text{Fe}^{2+}$  of increasing temperature like as sol-gel coating.<sup>11-13)</sup> It should be noted that  $\text{Fe}^{2+}$  is much more unstable than of  $\text{Fe}^{3+}$  at the high temperature. Moreover, the sol-gel coating method is not yet economically practical.

In this study, we report for the first time a nano sized  $\text{Al}_2\text{O}_3$ -coated  $\text{LiFePO}_4$  composite using a dry coating method. Dry coating refers to techniques where the core materials are strongly surrounded by fine particles through high impact collision without the need to increase temperature. Therefore, to retain discharge capacity and enhance electronic conductivity, surface modification of the particle using dry coating has been adapted in this work. These studies reveal that the surface modification of the cathode materials, by coating thin layers of  $\text{Al}_2\text{O}_3$ , increases high discharging capacity charge/discharge rates and decreases area-specific impedance (ASI).  $\text{Al}_2\text{O}_3$  was chosen for coating the particles as it has a high electronic conductivity and good stability with the electrolyte.<sup>14)</sup>

## 2. Experimental

### 2.1. Coating process

In this present study, a simple sol-gel process was adapted in order to synthesis  $\text{LiFePO}_4$  from lithium acetate dihydrate [ $\text{Li}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$ ], ammonium iron(II) sulfate [ $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$ ], phosphoric acid [ $\text{H}_3\text{PO}_4$ ], and sucrose [ $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ]. Sucrose and stoichiometric amounts of Fe, P, and Li were dissolved in distilled water at a molar ratio of 0.1 : 1 (sucrose :  $\text{LiFePO}_4$ ) and continuously stirred at  $80^\circ\text{C}$  for 4 h until a transparent sol was obtained. The sol was heated at  $100^\circ\text{C}$  for 3 h to remove the water, turning the sol into a viscous brown gel. This gel was heated at  $500^\circ\text{C}$  for 5 h in an argon atmosphere, and then calcined at  $800^\circ\text{C}$  for 10 h in an argon atmosphere to obtain  $\text{LiFePO}_4$  powder. The detailed preparation procedure and results have been previously submitted.<sup>15)</sup>

The starting coating material used in this study was alumina powder ( $\text{Al}_2\text{O}_3$  : Aldrich : 99.9% : < 10 nm). The powder mixture (100 g), consisting of a  $\text{LiFePO}_4$  to  $\text{Al}_2\text{O}_3$  ratio of 97 : 3 by weight, were mechanically processed using an attrition type device (Mecahno-fusion system; Hosokawa Micron Corp., Osaka, Japan). The device had a rotating chamber and a cooling system to prevent increasing temperatures. When the chamber rotated, the powder mixture was compressed under received various kinds of mechanical forces, such as compression and shearing, without any ball media. In this study chamber,

the rotating speed was set at 5,000 rpm. for 1 h throughout the experiment.

### 2.2. Material characterization

The X-ray diffraction patterns of the cathodes were obtained using a Bruker D8 diffractometer in the  $2\theta$  range from  $10$  to  $70^\circ$  with  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5406\text{\AA}$ ). The surface morphology of the coated powder was observed with a transition electron microscope (TEM).

To prepare the positive electrode, 80%  $\text{LiFePO}_4$  powder, 10% super-P carbon black (Aldrich), *N*-methyl-2-pyrrolidone, and 10% PVdF (Kureha KF100) binder were added in a crucible. After two hours of grinding, the viscous slurry was coated on aluminum foil using a doctor blade to make a film with a uniform thickness. The film was then dried at  $60^\circ\text{C}$  for 6 h and  $120^\circ\text{C}$  for 6 h in a vacuum oven. The thickness of the cathode film was approximately  $40\ \mu\text{m}$ . The CR2016 type coin cell was assembled in a glove box using the above cathode film, lithium, a porous polyethylene film, and a 1.2 M  $\text{LiPF}_6$  solution in a 1 : 1 : 3 volume ratio of ethylene carbonate (EC)/poly carbonate (PC)/dimethyl carbonate (DMC). The lithium metal foil was used as both the counter and reference electrode. After the coin cell assembly, the test cells were charged and discharged galvanostatically between 2.5 and 4.2 *versus*  $\text{Li}/\text{Li}^+$ , at a constant current density ( $170\ \text{mA g}^{-1}$  was assumed to be 1C rate). The cyclic voltammetry (CV) curves were obtained at  $0.1\ \text{mVs}^{-1}$  and between 2.5-4.2 V. All the electrochemical measurements were carried out at  $25^\circ\text{C}$ .

## 3. Results

### 3.1. Surface morphology characterization

There were three main approaches to coating, the principles of which are summarized in Fig. 1:

(1) **Sol-gel coating:** The coating material and core particle were dissolved in a solvent and the organic materials evaporated after heat treatment (Fig. 1a). The main drawbacks of this approach were the emission of heat and formation of a dense coating layer. The emission of heat can deteriorate the  $\text{Fe}^{2+}$  of the core particle while the dense coating layer can play a role as a Li ion blocking.

(2) **Dry coating:** Dry particle coating, as shown in Fig. 1b, consists of coating relatively large particle sizes (core material) with fine particles (coating material) using mechanical force, with no wetting. This leads to coated particles that could be quickly wetted in electrolyte and to faster Li ion (electron) movement because of their high porosity

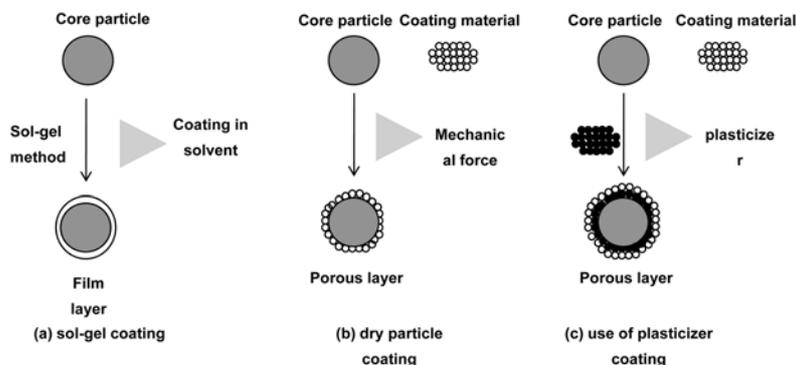


Fig. 1. Principles of different coating approaches.

(3) **Use of plasticizer coating:** Coating with the plasticizer consists of fixing fine particles on the core, using a non-aqueous binder or plasticizer (Fig. 1c), instead of mechanical force. The main drawbacks of this approach are the blocking of Li and the electrons of the plasticizer that leads to deterioration in electrochemical properties.

Our research concentrated on the second coating technique (dry coating), the objective being to compare bare cathode material with core-shell by dry coating. The HRTEM (high-resolution TEM) image of  $\text{LiFePO}_4$  is presented in Fig. 2. The average particle size of the samples lies in a range 200–600 nm in the previous measurements.<sup>15</sup> The surface of the bare sample particles was found to be smooth, whereas the surface of the coated  $\text{LiFePO}_4$  particle was found to be covered with a thin coating layer with a thickness of approximately 1–10 nm. This layer was not smooth, but uniform. The coating materials could be seen to be form compact, porous, and continuous films on the cathode material.

### 3.2. Electrochemical behavior

Cyclic voltammetry is a complementary and well-suited

technique to evaluate the cathodic performance and electrode kinetics of oxide materials. The cyclic voltammograms (CV) of the bare and  $\text{Al}_2\text{O}_3$ -coated  $\text{LiFePO}_4$  cathodes were recorded for cells at room temperature in the range of 2.5–4.2 V, with metallic lithium as the counter and reference electrodes. The CV at a scan rate of 0.1 mV/s is shown in Fig. 3. The important feature was the difference between the first and subsequent cycles. In the case of the bare  $\text{LiFePO}_4$  cathode, the anodic scan has one oxidation peak, a peak centered at 3.748 V, while the cathodic scan had one reduction peak, a minor one at 4.6 V centered at 3.154 V. The effect of the  $\text{Al}_2\text{O}_3$  coating was clearly revealed in the CV presented in Fig. 3. The first anodic scan had one oxidation peak, a major peak centered at 3.658 V, and a cathodic peak at 3.281 V, lower than to that of the bare compound. In addition, the peak was dramatically sharp compared to the uncoated one. This phenomenon indicated that the nano-sized  $\text{Al}_2\text{O}_3$  coating results were negligible towards polarization during intercalation/de-intercalation.

Typical initial charge and discharge curves of cathodes for the bare and the  $\text{Al}_2\text{O}_3$ -coated  $\text{LiFePO}_4$  cell, containing a 1.2 M  $\text{LiPF}_6$ -EC/PC/DMC (1 : 1 : 3) at a constant

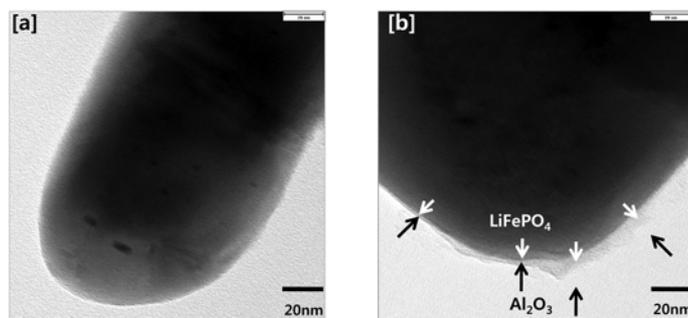


Fig. 2. TEM image of (a) bare (b) 3 wt.%  $\text{Al}_2\text{O}_3$  coated  $\text{LiFePO}_4$  compound.

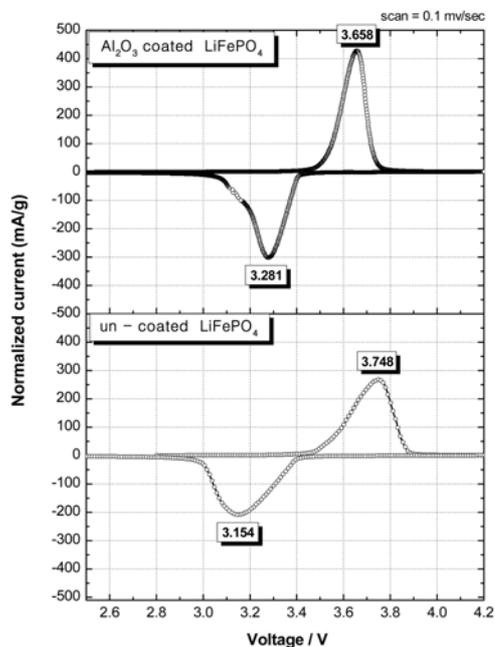


Fig. 3. Cyclic voltammetry of bare and 3 wt.%  $\text{Al}_2\text{O}_3$  coated  $\text{LiFePO}_4$  cell between 2.5 and 4.2 V at a scan rate of  $0.1 \text{ mVs}^{-1}$ .

current density ( $85 \text{ mA/g}$ ), are shown in Fig. 4. These curves show that the cathode polarization for both charge and discharge was reduced substantially by the  $\text{Al}_2\text{O}_3$  coating. The charge-discharge capacity was slightly decreased ( $9 \text{ mAh}$ ) by the coating due to adding  $\text{Al}_2\text{O}_3$  material ( $3 \text{ wt}\%$ ), which is inactive towards Li.

Fig. 4 shows the discharge capacity and cyclic performance cathodes for the bare and the  $\text{Al}_2\text{O}_3$ -coated  $\text{LiFePO}_4$  electrodes as a function of the charge-discharge rates. The measurements were carried out at  $0.1\text{C}$ ,  $0.2\text{C}$ ,  $0.5\text{C}$ ,  $1\text{C}$ ,  $2\text{C}$ ,  $5\text{C}$ , and  $0.1\text{C}$  rates in the voltage range of  $2.5\text{--}4.2 \text{ V}$ . The discharge capacity of the  $\text{LiFePO}_4$  electrodes was clearly enhanced by  $\text{Al}_2\text{O}_3$  coating at high C rates, particularly above a rate of  $1\text{C}$ . Therefore, the  $\text{Al}_2\text{O}_3$  coating effectively improved the rate capability of the  $\text{LiFePO}_4$  cathode. This coated layer minimized cell polarization due to its high electronic conductivity, which is especially important at high C rates. Minimized cell polarization can be also observed by cyclic voltammograms in Fig. 3 and the charge-discharge curve in Fig. 4.

The area specific impedance (ASI) was measured as a function of the depth of discharge (DOD) in order to understand the superior electrochemical properties of the carbon-coated  $\text{LiFePO}_4$  cell. During the lithium insertion/

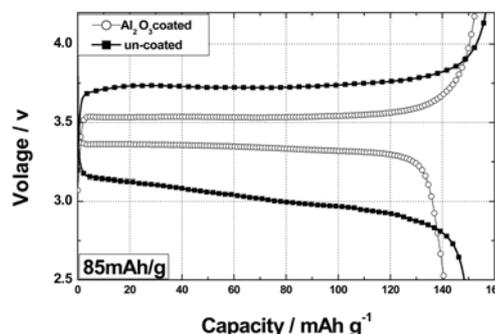


Fig. 4. First charge-discharge curves of bare and  $3 \text{ wt}\%$   $\text{Al}_2\text{O}_3$  coated  $\text{LiFePO}_4$  cell at a current density of  $0.5\text{C}$  ( $85 \text{ mA/g}$ ).

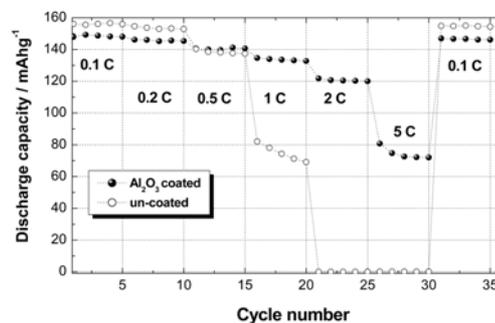


Fig. 5. Discharge capacities and cyclic performances of bare and  $3 \text{ wt}\%$   $\text{Al}_2\text{O}_3$  coated  $\text{LiFePO}_4$  cell in the voltage range of  $2.5\text{--}4.2 \text{ V}$  at  $0.1$ ,  $0.2$ ,  $0.5$ ,  $1$ ,  $2$ ,  $5$ , and  $0.1\text{C}$  rates.

extraction, a combination of electrode kinetics, the ohmic drop, and the  $\text{Li}^+$  ion diffusion caused a change in the overall cell voltage.<sup>16)</sup> The area specific impedance (ASI) was determined using the equation:  $(A \cdot \Delta V) / I$ ,<sup>17)</sup> where  $A$  is the cross-sectional area of the electrode ( $1.0 \text{ cm}^2$ ),  $\Delta V$  the voltage variation during the current interruption for  $60 \text{ s}$  at each DOD, and  $I$  the constant current density of  $0.1 \text{ mA/cm}^2$  (the thickness of the cathode film was approximately  $40 \mu\text{m}$ ). In Fig. 6, the  $\text{Al}_2\text{O}_3$ -coated  $\text{LiFePO}_4$  cathode ( $500\text{--}900 \Omega\text{cm}^2$ ) exhibited much lower ASI values than that of an un-coated  $\text{LiFePO}_4$  cathode ( $2500\text{--}3500 \Omega\text{cm}^2$ ). Again, the improved ASI characteristics were ascribed to the reduced interfacial impedance between cathode and electrolyte, which confirmed that the  $\text{Al}_2\text{O}_3$ -coated layer on the surface of the  $\text{LiFePO}_4$  cathode acted as an interfacial stabilizer and electronic conductor. A continuous conducting coating layer was formed on the surface of  $\text{LiFePO}_4$  particles, resulting in a very significant increase in electro-active zones. However, the mechanisms involved with the  $\text{Al}_2\text{O}_3$  coating, such as interactions with the electrolyte, still require identification.

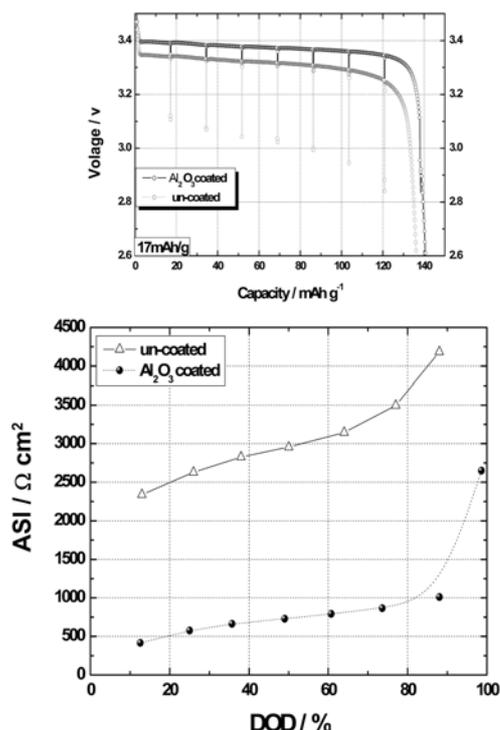


Fig. 6. Area specific impedance (ASI) of bare and Al<sub>2</sub>O<sub>3</sub> coated LiFePO<sub>4</sub> cell as a function of state of discharge (DOD).

#### 4. Conclusions

A significant improvement in capacity and cycle stability at high charge/discharge rates ( $> 1C$ ) were achieved by nano-sized Al<sub>2</sub>O<sub>3</sub> coatings using a novel dry coating method. A continuous and porous layer was formed on the surface of the LiFePO<sub>4</sub> particles, as corroborated by the HRTEM results. XRD analysis showed that the coating layer of the sample was in an amorphous phase. The cyclic voltammogram and ASI measurements indicate that the cathode polarization for both charge and discharge was reduced substantially by the Al<sub>2</sub>O<sub>3</sub> coating. The highly improved electrochemical performance of the Al<sub>2</sub>O<sub>3</sub>-coated LiFePO<sub>4</sub> electrode was partly attributed to the increase in the electrical contact between the cathode grains and minimization of the interfacial resistance by a uniform and porous Al<sub>2</sub>O<sub>3</sub> coating, which is electronically conductive.

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