The Origin of the Residual Carbon in LiFePO₄ Synthesized by Wet Milling

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This study reports the origin of the electrochemical improvement of LiFePO₄ when synthesized by wet milling using acetone without conventional carbon coating. The wet milled LiFePO₄ delivers 149 mAhg⁻¹ at 0.1 C, which is comparable to carbon coated LiFePO₄ and approximately 74% higher than that of dry milled LiFePO₄, suggesting that the wet milling process can increase the capacity in addition to conventional carbon coating methods. UV spectroscopy, elemental microanalysis, and evolved gas analysis are used to find the root cause of the capacity improvement during the mechanochemical reaction in acetone. The analytical results show that the improvement is attributed to the conductive residual carbon on the surface of the wet milled LiFePO₄ particles, which is produced by the reaction of FeC₂O₄·2H₂O with acetone during wet milling through oxygen deficiency in the precursor.

Key Words: Lithium iron phosphate, Wet milling, Mechanochemical reaction, Rate capability, Carbon coating

Introduction

Lithium-ion batteries using an olivine-type lithium iron phosphate (LiFePO₄) cathode have attracted much attention as a power source for electric and hybrid electric vehicles due to its low material cost, non toxicity, and better thermal stability. However, the commercial application of LiFePO₄ as a cathode for lithium secondary batteries has been limited because of its low electrical conductivity and poor rate capability. Recent research efforts have focused on improving the electrical conductivity of LiFePO₄ by coating carbonaceous conductors and doping with metallic elements such as Cr, Mg, Ni, or Co. Ravet et al. coated LiFePO₄ using sucrose, cellulose acetate, and a modified polyacrylic and achieved the initial discharge capacity up to 140 mAhg⁻¹. Prosini et al. investigated LiFePO₄ coated with 10 wt % carbon black and obtained initial capacity up to 120 mAhg⁻¹. Chung et al. reported that electrical conductivity of LiFePO₄ was enhanced by metal doping and the doped cathode delivered 140 mAhg⁻¹ at 0.1 C. Wang et al. also reported the enhancement of rate performance of LiFePO₄ by metal doping without increasing the initial capacity. They suggested that the initial capacity is mainly improved by increasing the electrical conductivity of the LiFePO₄, while the rate performance could be enhanced by metal doping. On the other hand, it was also suggested that the electrical conductivity of LiFePO₄ could be improved by the presence of residual carbon after synthesis. Meligrana et al. found that residual carbon can be obtained after mild hydrothermal synthesis employing hexadecyltrimethylammonium bromide (CTAB). It would, therefore, seem that the initial capacity of the LiFePO₄ could be improved without rigorous carbon coating, if the mechanochemical reaction could produce carbonaceous by-products during the wet milling process. However, there is no detailed investigation about the possible formation of the carbonaceous products during wet milling and their effects on the electrochemical properties of the LiFePO₄.

This study focused on the root cause of the enhancement of rate performance and initial capacity of LiFePO₄ when acetone was used for the homogeneous mixing during milling. Evolved gas analysis (EGA), elemental microanalysis, and UV spectroscopy were employed to investigate the mechanochemical reaction of the precursors with acetone, which produced the carbonaceous byproducts and improved the electrochemical response during charge-discharge of the lithium secondary batteries.

Experimental Details

The mixture of Li₂CO₃ (Aldrich, ≥99%), FeC₂O₄·2H₂O (Aldrich, ≥99%), and (NH₄)H₂PO₄ (Aldrich, ≥99%) was placed in a zirconia bowl with the molar ratio of 1:2:2 and mechanochemical reaction was carried out for 3 hours using a planetary mill (FRITSCH Pulverisette 5) with a ball-to-powder weight ratio of 20:1. The rotating speed was set at 250 rpm for dry milling and 400 rpm for wet milling to compensate the damping effect from acetone. 400 rpm for dry milling showed the segregation of starting materials, 250 rpm for wet milling showed low crystallinity of LiFePO₄. The mixture obtained from planetary milling was heat treated at 600 °C using a tube furnace for 10 h under Ar + 5% H₂ atmosphere. Evolved gas analysis (EGA; Py-2020iD, Frontier lab, Japan, and 6890N GC/5975i MS, Agilent, USA) was carried out to examine the gaseous products during the heat treatment. The wet milling media after the milling process was analyzed by an ultraviolet-visible spectrophotometer (UV: S-3100, Scinco, Korea). For UV analysis, each starting material was milled in acetone at the same condition as LiFePO₄ and the acetone was retrieved after milling to analyze using UV spectroscopy.

The crystal structure of LiFePO₄ was examined by X-ray diffraction (XRD; D/MAX-II A) with Cu Kα in a scan range of...
The Origin of the Residual Carbon

The cathodes were prepared by slurring the active material with 5 wt % polyvinylidene fluoride and 10 wt % acetylene black (w/w) in an n-methyl pyrrolidone solvent. The mixture was coated onto an Al foil and dried at 80 °C in a ventilation oven. After drying, the cathodes were held in a vacuum oven at 80 °C for 12 h. The cathode was 60 μm thick and contained approximately 5 ~ 7 mg cm\(^{-2}\) of the active material. The charge and discharge characteristics of the cathode were examined by a field emission scanning electron microscope (FE-SEM, Hitachi, S-4300, Japan) and TEM (JEOL, JEM-2100F, Japan). TEM specimen was prepared by dropping a dilute ethanol solution containing LiFePO\(_4\) particles on a Cu grid. The amount of residual carbon in the LiFePO\(_4\) was measured by elemental analyzer (ThermoFinnigan, Flash EA 1112, Italy).

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Results and Discussion

The structure and average particle size of wet and dry milled LiFePO\(_4\) were examined using XRD since they can strongly affect the electrochemical performance during charge and discharge cycles. Fig. 1 shows XRD patterns obtained from the LiFePO\(_4\) particles after the heat treatment at 600 °C. Both patterns showed typical diffraction peaks corresponding to LiFePO\(_4\). The lattice parameters calculated from the XRD patterns were same regardless of the milling condition (Table 1). The particle sizes of both specimens were calculated from the full-width at half maximum (FWHM) of the diffraction peaks in Fig. 1. The average sizes (D) of the wet and dry milled LiFePO\(_4\) crystallites were 40.55 nm and 40.48 nm, respectively, which was estimated from the Scherrer’s formula described by:

\[
D = \frac{0.9\lambda}{\beta \cos \theta}, \quad \text{where } \lambda = 1.5418 \text{ Å (Cu Kα)} \text{ and } \beta \text{ is FWHM at the diffraction angle of } \theta.
\]

The LiFePO\(_4\) particles produced from wet and dry milling were also examined using SEM to confirm particle size distribution and to study possible byproducts produced during synthesis. Fig. 2 shows secondary electron images of (a) wet and (b) dry milled LiFePO\(_4\) particles. Particle surfaces were clean when dry milling was carried out without a milling agent, while clusters of small particles were observed on the surface when the acetone was used as a milling agent. The adherent particles on the surface of the wet milled LiFePO\(_4\) seemed to be attributed to the milling agent (acetone) during wet milling at a higher rotating speed (400 rpm). This is because the fast rotating speed provides high energy to accelerate the mechanochemical reaction of acetone with starting materials, which can induce the formation of new reaction products.

The same LiFePO\(_4\) particles were also investigated by TEM at higher magnifications to analyze the adherent particles. Fig. 3 shows TEM micrographs of LiFePO\(_4\) particles produced from wet and dry milled LiFePO\(_4\). They showed clean surfaces with clear phase contrast when it was dry milled, while the wet milled LiFePO\(_4\) showed adherent phases in the LiFePO\(_4\) particles (Fig. 3). Elemental analysis was also carried out to examine carbon content in the LiFePO\(_4\) particles produced by dry and wet milling processes. The results from the elementary anal-

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**Figure 1.** XRD patterns of wet milled and dry milled LiFePO\(_4\).

**Figure 2.** SEM images of (a) wet milled and (b) dry milled LiFePO\(_4\).

**Figure 3.** High resolution TEM images of (a) wet milled and (b) dry milled LiFePO\(_4\).

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<table>
<thead>
<tr>
<th>Wet milled LiFePO(_4)</th>
<th>10.3016</th>
<th>5.9939</th>
<th>4.6898</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry milled LiFePO(_4)</td>
<td>10.3121</td>
<td>5.9927</td>
<td>4.6830</td>
</tr>
</tbody>
</table>

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Table 1. Lattice parameters of wet milled and dry milled LiFePO\(_4\)
ysis showed that carbon content of particles from wet milling was approximately 4 times greater than that from dry milling (Table 2). Using the wet and dry milled LiFePO₄, the initial capacity during discharge was measured to examine the possible effects of acetone on electrochemical performance. Fig. 4 shows the specific capacity of dry and wet milled LiFePO₄ up to 50 cycles. The initial capacity of the dry milled LiFePO₄ delivered 68 mAh g⁻¹ at 0.2 C, which was similar to that of bare LiFePO₄. On the other hand, wet milled LiFePO₄ delivered much improved initial capacity of 143 mAh g⁻¹ at 0.2 C and this was comparable to the carbon-coated LiFePO₄. This suggests that the carbonaceous product produced on the particle surface during wet milling plays a similar role as the conductive layer from the conventional carbon coating LiFePO₄. The initial capacity of LiFePO₄ improved by carbon coating has been reported by others and they are compared in the Table 3. The table indicates that the carbon layer on the particle surface, which was produced by wet milling, increases electrical conductivity of LiFePO₄ and initial capacity. Fig. 4 also indicated that the wet milled LiFePO₄ retained 99% of the initial capacity after 50 cycles at 0.2 C, whereas the dry milled LiFePO₄ showed only 88% capacity retention. It suggested that the residual carbon from wet milled precursor not only enhanced the capacity of LiFePO₄ but also improved cyclability. Although the amount of residual carbon was smaller than the carbon coated by other conventional methods, it was noteworthy to find a similar level of capacity retention.

Several researches have been carried out conventional carbon coating by using milling agents. Dong et al. reported carbon coated LiFePO₄ delivering 156 mAh g⁻¹ of the initial capacity by using acetone as a milling agent. Yang et al. reported 158 mAh g⁻¹ of initial capacity for LiFePO₄/polyacenes milled with ethanol. Zhang et al. reported carbon coated LiFePO₄ with ethanol by using conventional carbon coating method. Initial capacity of LiFePO₄ was 145.5 mAh g⁻¹ at 0.5 C which was similar value compared to our experiment. These experiments also could be affected by the residual carbon effect due to the milling agent. We also have synthesized the LiFePO₄ with acetone, ethanol, and methanol without additive carbon sources. Electrochemical performances of those samples showed similar values suggesting residual carbon was obtained by the milling agents. The amount of carbon in LiFePO₄ was compared to examine their cyclability at high C rates. Fig. 5 shows the specific capacity when the charge-discharge rate is increased from 0.1 to 20 C. At 5 C, the capacity of the dry milled LiFePO₄ delivered almost no current, while wet milled LiFePO₄ maintained approximately 50% of the initial capacity (75 mAh g⁻¹). The poor charge-discharge performance of the dry milled LiFePO₄ at high C rates is attributed to high electrical resistance and high polarization. However, both specimens showed almost no current at higher charge-discharge rates over 10 C. This indicated that the residual carbon on the particle surface from wet milling was not sufficient to sustain the cyclability over 10 C, suggesting further treatments such as a doping with metallic elements was needed to retain good performance at high C rates. Fey et al. also reported the similar capacity degradation of carbon coated LiFePO₄ at high C rates.

The charge-discharge characteristics of the wet and dry milled LiFePO₄ were also examined (Fig. 6). This is because the length of the plateau indicates the operation capacity, with a longer plateau being of great advantage for a longer cell operation. The figure showed that the wet milled LiFePO₄ exhibited a longer plateau than that of the dry milled LiFePO₄, indicating that the wet milled LiFePO₄ delivered more capacity. It also indicated that the wet milled LiFePO₄ was charged at lower voltage than that of the dry milled LiFePO₄. This is another evidence for enhancing the electrical conductivity of wet milled LiFePO₄ since low voltage is needed to produce a constant current when charging.

In order to find the source of the extra carbon in the LiFePO₄ particle produced after wet milling, evolved gas analysis was carried out using the wet and dry milled precursors before heat-treatment (Fig. 7). The different profiles in the figure indicated that the precursors had dissimilar chemical states after wet or

### Table 2. The amount of carbon in LiFePO₄

<table>
<thead>
<tr>
<th>Materials</th>
<th>Wet milling</th>
<th>Dry milling</th>
</tr>
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<tbody>
<tr>
<td>Carbon (wt %)</td>
<td>2.08</td>
<td>0.47</td>
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</table>

### Table 3. Comparison of initial capacity at 0.1 C

<table>
<thead>
<tr>
<th>Materials</th>
<th>Graphite 0.1 C [22]</th>
<th>Carbon black 0.1 C [22]</th>
<th>Acetylene black 0.1 C [22]</th>
<th>Sucrose 0.143 C [12]</th>
<th>Wet 0.1 C</th>
<th>Dry 0.1 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial capacity (mAh g⁻¹)</td>
<td>141</td>
<td>140</td>
<td>138</td>
<td>120</td>
<td>143.48</td>
<td>82.24</td>
</tr>
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</table>
dry milling. The analysis of the evolved gas showed that the main gaseous species were CO and CO$_2$ and their ratio was higher (CO/CO$_2$ = 0.22) in the case of wet milled precursors than dry precursors (CO/CO$_2$ = 0.13). This indicates that the wet milled precursors generated more CO gas since it contains less oxygen. The oxygen deficiency in the wet milled precursor induced the formation of residual carbon during heat treatments since the carbon atoms in the precursor molecules were not removed as gases. In particular, the profiles from wet milled precursor exhibited a peak near 220°C, which was consisted of high molecular weight gases (M$_w$ = 120), suggesting possible reaction products produced by the reaction of acetone with the precursors. The amount of residual carbon as changing the acetone content was not investigated. However, since the amount of residual carbon was determined by starting materials contents, the increment of the acetone content would not affect on the residual carbon content unless too small amount of acetone was used.

In order to find the possible precursors that could be reacted by the acetone during wet milling, UV spectroscopy was employed. The spectrum of the acetone after milling the precursor showed intensity peaks in the range of wavelength between 270 - 320 nm (Fig. 8). The UV spectrum obtained from the acetone milled with FeC$_2$O$_4$·2H$_2$O showed peaks similar to those from the acetone after milling the three precursors. On the other hand, Li$_2$CO$_3$ and (NH$_4$)H$_2$PO$_4$ showed relatively small peaks in their spectra, suggesting that the major peaks in the spectra obtained from acetone after wet milling were mainly originated from the reaction of FeC$_2$O$_4$·2H$_2$O with acetone. As shown in the Fig. 9, the color of the acetone after milling with precursors also indicated that the main reaction with acetone was done by the precursor for an iron source, indicating that the high mole-
cular weight gas evolved at 220 °C during EGA analysis of the wet milled precursor is attributed to the reaction product of FeC₂O₄·2H₂O with acetone, which induced oxygen deficiency and followed by the formation of carbonaceous material during heat treatment. The further studies were needed to investigate the exact reaction product and the reaction mechanism between FeC₂O₄·2H₂O and acetone. This is a salient result because the carbonaceous byproducts produced during the mechanochemical properties of LiFePO₄.

Wet and dry milled LiFePO₄ were prepared to compare their electrochemical properties without conventional carbon coating. Despite the use of the same starting materials for the LiFePO₄ synthesis, the morphology and electrochemical properties were different due to the acetone used for wet milling. Residual carbon was found on the surface of the wet milled LiFePO₄ particles, which was originated from oxygen deficiency in the precursor. The oxygen deficiency was attributed to the reaction of FeC₂O₄·2H₂O with acetone during wet milling and it induced the formation of carbonaceous materials on the particle surface. Initial capacity of wet milled LiFePO₄ was about 149 mAhg⁻¹ which was comparable to the capacity obtained from other carbon coated LiFePO₄. Rate capability of wet milled LiFePO₄ was 75 mAhg⁻¹ at 5 C, while dry milled LiFePO₄ delivered almost no current, suggesting that the residual carbon, produced by reaction of acetone with precursor, was attributed to the capacity enhancement.

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References