Tailoring Crystal Structure and Morphology of LiFePO$_4$/C Cathode Materials Synthesized by Heterogeneous Growth on Nanostructured LiFePO$_4$ Seed Crystals

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ABSTRACT: Porous and coarse (5–10 μm) LiFePO$_4$/C composites with excellent electrochemical performance were synthesized by a growth technology using nanostructured (100–200 nm) LiFePO$_4$ as seed crystals for the 2nd crystallization process. The porous and coarse LiFePO$_4$/C presented a high initial discharge capacity (~155 mA h g$^{-1}$ at 0.1 C), superior rate-capability (~100 mA h g$^{-1}$ at 5 C, ~65 % of the discharge capacity at 0.1 C), and excellent cycling performance (~131 mA h g$^{-1}$, ~98 % of its initial discharge capacity after 100 cycles at 1 C). The improvement in the rate-capability of the LiFePO$_4$/C was attributed to the high reaction area resulted from the pore tunnels formed inside LiFePO$_4$ particles and short Li-ion diffusion length. The improved cycling performance of the LiFePO$_4$/C resulted from the enhanced structural stability against Li-deficient LiFePO$_4$ phase formation after cycling by the expansion of the 1D Li-ion diffusion channel in the LiFePO$_4$ crystal structure.

KEYWORDS: lithium iron phosphate, porous, seed crystals, heterogeneous particle growth, lithium-ion batteries

1. INTRODUCTION

LiFePO$_4$, with an ordered olivine structure is considered one of the most promising cathode materials for large-sized Li-ion batteries due to its excellent structural stability at elevated temperatures, high reversibility of Li-ion insertion/extraction, low cost of starting materials, and nontoxicity. However, despite the numerous merits of LiFePO$_4$, its practical application has been limited by its inherently poor kinetic properties caused by low electronic and ionic transfer. However, recent approaches to improve the kinetic properties of LiFePO$_4$ has been accomplished by carbon coating (LiFePO$_4$/C composite), particle size reduction to the nanoscale, and heteroatom doping. However, the gravimetric/volumetric energy density of a nanostructured LiFePO$_4$ electrode is inevitably reduced because the tap density of a LiFePO$_4$ electrode decreases as the LiFePO$_4$ particle size approaches the nanoscale, and the mass fraction of bulky and inactive conducting carbons increases to secure the electrical contact between the LiFePO$_4$ nanoparticles. Thus, it is essential to develop high-performance LiFePO$_4$/C composites with high energy density or high tap density.

To realize high power LiFePO$_4$/C composites with no expense of energy density, the following requirements must be taken into consideration: (i) the microscale size of LiFePO$_4$ particles, (ii) a large electrode/electrolyte interface area to decrease the applied current density per unit surface area, (iii) the particle morphology to reduce the Li-ion diffusion length in LiFePO$_4$ particles, and (iv) the uniform distribution of conductive carbons to increase the electronic conductivity of LiFePO$_4$ Thus, porous and coarse LiFePO$_4$/C, which exists as clusters comprised of nano- or sub-microsized LiFePO$_4$ primary particles, has been suggested by several research groups. However, unlike previous studies on the synthesis of LiFePO$_4$/C that use common synthetic routes (e.g., co-precipitation, spray pyrolysis, and the hydrothermal process), porous and coarse LiFePO$_4$/C was obtained here by a simple and novel growth technology using LiFePO$_4$ nanocrystals as seed crystals.

The schematic illustration for the formation of porous and coarse LiFePO$_4$/C, proposed in this study, is presented in Figure 1. First, nanoscale (100–200 nm) LiFePO$_4$ crystals are used as seed crystals for the 2nd crystallization process. The seed crystals are uniformly mixed with additional Li, Fe, P precursors and sucrose in a solvent, and then the collected mixed powders are heat-treated for crystallization.
anticipate that the existing LiFePO₄ seed crystals will act as heterogeneous nucleation sites for the 2nd crystallization of LiFePO₄, thereby forming uniform and coarse particles with high tap density. Further, the gas evolved from the carbonaceous reaction during the heat treatment or mismatched neighboring crystals that have grown on the seed crystals would form pore tunnels into the coarse LiFePO₄/C particles, through which electrolyte may directly be in contact with the inside of the particle for improving reaction kinetics in Li-ion insertion/extraction.

Thus, the research objective of this study is to investigate the morphology and electrochemical performance of the porous and coarse LiFePO₄/C composite synthesized by a growth technology using nanostructured (100–200 nm) LiFePO₄ as seed crystals for the 2nd crystallization process.

2. EXPERIMENTAL SECTION

2.1. Material Preparation and Characterization. Porous and coarse LiFePO₄/C composites were synthesized by a growth technology using commercial nanoscale (100–200 nm) LiFePO₄ crystals as heterogeneous nucleation sites for the growth of LiFePO₄ to coarse particle clusters. The LiFePO₄ seed crystals were dispersed in a deionized (DI) water/ethanol mixed solution in which sucrose (3 wt %) was dissolved, and then Li, Fe, P precursors (LiNO₃, FeSO₄·7H₂O, and NH₄H₂PO₄) were added to the solution. The weight ratio between the seed crystals and the expected total amount of LiFePO₄ powder was 1:2 (w/w). The precursor mixture was stirred for 6 h with N₂ bubbling and then dried at 120 °C in a vacuum oven to prevent the oxidation of ferrous ions (Fe²⁺) in FeSO₄·7H₂O. The end product, LiFePO₄/C, was obtained by crystallization at 650 °C for 10 h in 5 wt % H₂ + N₂ mixed gas flow. The morphology of the LiFePO₄ seed crystals and LiFePO₄/C was characterized by scanning electron microscopy (SEM, Philips, XL30SFEG) and transmission electron microscopy (TEM, Philips, Tecnai G2 F30 S-TWIN, 300 kV). The crystal structures of the LiFePO₄ seed crystals and LiFePO₄/C were confirmed by X-ray powder diffraction (XRD, Rigaku D/MAX-IIIIC, 3 kW) and high-resolution powder neutron diffraction (HRPD, high-resolution powder diffractometer at the Hanaro Center of the Korea Atomic Energy Research Institute), and the combined Rietveld refinements for the XRD and HRPD patterns were conducted. Herein, structural refinement cycles included zero-point shift, scale factor, lattice parameters, and background parameters as variables. Following satisfactory matching of the peak positions, the atomic positions, thermal parameters, and peak profile parameters, including the peak asymmetry, were refined. The residual carbon content in LiFePO₄/C composites was measured with an element analyzer (EA, CE Instruments, EA1110-FISONS), and Brunauer-Emmett-Teller (BET) surface area and pore size/volume analysis was performed using a surface area analyzer (BET, BEL Japan Inc., BELSORP-max). To estimate the tap density of the LiFePO₄ seed crystals and LiFePO₄/C, the materials (0.75 g) were put into a measuring cylinder and tapped for 5 min.²⁰

2.2. Cell Fabrication and Electrochemical Analysis. To fabricate the electrode, a mixture of 75 wt % of each active material and 17 wt % acetylene black was added to N-methyl-2-pyrrolidene (NMP) solvent containing 8 wt % polyvinylidene fluoride (PVdF). This slurry was pasted onto an Al foil substrate and then dried at 120 °C in a vacuum oven. The dried paste was pressed and then punched into a disc shape with a diameter of 1.3 cm. The electrochemical properties of the prepared electrodes were evaluated using 2016 coin-type cells that were assembled in an Ar-filled glove box. Li-metal foil (Cyprus Foote Mineral, 99.98%) was used as a counter electrode, and 1 M LiPF₆ dissolved in 1:1 (v/v) ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as the electrolyte. The charge/discharge characteristics of the fabricated cells were measured with a battery cycler (Toscat-3100u, Toyo System). For the initial two cycles, the cells were charged at a constant current density of 0.1 C until 4.3 V (vs Li⁺/Li) and were continuously applied at a constant voltage of 4.3 V until a capacity of 0.05 C and then discharged at a constant current density of 0.1 C until 2.5 V. From the 3rd cycle onward, the cells were charged and discharged (0.1 C) galvanostatically between 2.5 and 4.3 V. For convenience, the discharge capacity of the materials with cycling was collected from the 3rd cycle.

3. RESULTS AND DISCUSSION

Figure 2 exhibits the scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of commercial LiFePO₄ seed crystals, denoted as Seed-LFP and LiFePO₄/C composites prepared by a solution-based process and those formed by the growth technology using LiFePO₄ seed crystals, denoted as S-LFP/C and TS-LFP/C, respectively. The Seed-LFP have plate-shaped crystal with an average width of ∼100 nm and a length of ∼200 nm, as shown in Figure 2a,b. Figure 2c confirms that the S-LFP/C, synthesized by a solution-based process without the Seed-LFP, features irregularly shaped and coarse (∼10 μm) LiFePO₄ particles with smooth surfaces. However, the TS-LFP/C has relatively uniform, round, and
coarse (5−10 μm) LiFePO4 particles, each of which comprises a cluster of many LiFePO4 crystals grown on the seed crystals, as shown in Figure 2e,f. Moreover, contrary to the S-LFP/C, the TS-LFP/C has a substantial number of pore tunnels inside the particle (compare parts d and f of Figure 2). The most important point here is that the morphology of the TS-LFP/C is what we anticipated in developing the porous and coarse LiFePO4/C composite by the growth technology; that is, the as-prepared LiFePO4 seed crystals act as heterogeneous nucleation sites with formation of pore tunnels by evolution of carbonaceous gas in the 2nd crystallization process or by the mismatch space between neighboring crystals that have grown on the seed crystals.

The X-ray powder diffraction (XRD) patterns of the three prepared materials represented in Figure 3 show that the crystalline LiFePO4 seed crystals and LiFePO4/C composites were synthesized without appreciable impurity phases.

The physical characteristics (residual carbon content, BET surface area, pore volume, and tap density) of the Seed-LFP, S-LFP/C, and TS-LFP/C are given in Table 1. According to the results of element analysis (EA), the amount of residual carbon in the Seed-LFP is negligible, but 2.2−2.3 wt % carbon remains in the S-LFP/C and TS-LFP/C composites. The difference between the targeted (3 wt %) and actual carbon content in LiFePO4/C is due to the loss of carbons through carbothermal reactions at the LiFePO4 formation temperature (650 °C).

The BET surface area and the average pore volume of the materials were determined from the N2 adsorption/desorption isotherms of the particles. It is significant that in spite of the comparable actual carbon content in S-LFP/C and TS-LFP/C, the surface area (21.67 m2 g⁻¹) and pore volume (0.067 cm³ g⁻¹) of TS-LFP/C are much greater than those of S-LFP/C, which is consistent with the SEM and TEM results shown in Figure 2. The estimated tap density of the S-LFP/C and TS-LFP/C are ~0.95 g cm⁻³ and ~1.10 g cm⁻³, respectively, which are higher than that (~0.82 g cm⁻³) of the carbon-free nanoscale Seed-LFP. The relatively low tap density of the S-LFP/C compared with the TS-LFP/C might be attributed to

Figure 2. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of (a, b) Seed-LFP, (c, d) S-LFP/C, and (e, f) TS-LFP/C.
the irregular-shaped LiFePO$_4$ particles of the S-LFP/C, as shown in Figure 2c.

Figure 4a shows the initial galvanostatic voltage profiles of the Seed-LFP, S-LFP/C, and TS-LFP/C at a rate of 0.1 C. Though the Seed-LFP has nanosized LiFePO$_4$ particles, its discharge capacity is $\sim 110$ mA h g$^{-1}$, which is much lower than the theoretical discharge capacity ($\sim 170$ mA h g$^{-1}$) of LiFePO$_4$ because the electrical connection between the nanosized LiFePO$_4$ particles is not complete due to the deficiency of conducting carbons. In contrast, the compact S-LFP/C and the porous TS-LFP/C have high discharge capacities of $\sim 153$ mA h g$^{-1}$ and $\sim 155$ mA h g$^{-1}$, respectively. Given that half the total weight of the TS-LFP/C originates from the Seed-LFP, the high discharge capacity of the TS-LFP/C might result from the change in the morphology and carbon content from those in the Seed-LFP as presented in Table 1.

The rate-capabilities of the Seed-LFP, S-LFP/C, and TS-LFP/C are represented in Figure 4b. The discharge capacity of the S-LFP/C achieved at low current density (0.2 C and 0.5 C) is similar to that obtained at 0.1 C. However, an abrupt decrease in the discharge capacity of the S-LFP/C is observed with an increase in the current density (>0.5 C), which indicates that Li-ion insertion/extraction into/out of the LiFePO$_4$ particles is kinetically limited at a relatively high C-rate. On the other hand, the rate-capability of the TS-LFP/C is superior to that of the S-LFP/C. At the high current density of 5 C, the discharge capacity ($\sim 100$ mA h g$^{-1}$) of the TS-LFP/C is much higher than that of the S-LFP/C (6 mA h g$^{-1}$), which is attributed to the particle morphology of the TS-LFP/C characterized by the large reaction area due to its porous structure.

Table 1. Residual Carbon Content, BET Surface Area, Pore Volume, and Tap Density of the Seed-LFP, S-LFP/C, and TS-LFP/C

<table>
<thead>
<tr>
<th>samples</th>
<th>residual carbon content (wt %)</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>pore volume (cm$^3$ g$^{-1}$)</th>
<th>tap density (g cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seed-LFP</td>
<td>0.0560</td>
<td>19.0399</td>
<td>0.080</td>
<td>$\sim 0.82$</td>
</tr>
<tr>
<td>S-LFP/C</td>
<td>2.2892</td>
<td>7.4866</td>
<td>0.018</td>
<td>$\sim 0.95$</td>
</tr>
<tr>
<td>TS-LFP/C</td>
<td>2.2113</td>
<td>21.6683</td>
<td>0.067</td>
<td>$\sim 1.10$</td>
</tr>
</tbody>
</table>

Figure 3. X-ray powder diffraction (XRD) patterns for the Seed-LFP, S-LFP/C, TS-LFP/C, and ICSD (Inorganic Crystal Structure Database) reference pattern (no. 83-2092; triphylite LiFePO$_4$) in JADE software.

Figure 4c shows the cycling performance of the S-LFP/C and TS-LFP/C at 1 C. After 100 cycles, the TS-LFP/C exhibited a high discharge capacity of $\sim 131$ mA h g$^{-1}$, corresponding to $\sim 98\%$ of its initial discharge capacity ($\sim 137$ mA h g$^{-1}$), whereas the S-LFP/C showed a discharge capacity of $\sim 90$ mA h g$^{-1}$, $\sim 82.6\%$ of its initial discharge capacity ($\sim 109$ mA h g$^{-1}$).

Figure 5 presents the ex situ XRD patterns for the S-LFP/C and TS-LFP/C, respectively, after 100 cycles, which are compared with those in Figure 3. For the S-LFP/C electrode, its crystal structure has changed to a Li-deficient LiFePO$_4$ phase as confirmed by the peaks marked in Figure 5. In contrast, the TS-LFP/C electrode sustained its pristine crystal
structure. This result demonstrates that the significant capacity degradation in the S-LFP/C with cycling appears to be associated with a structural instability. From the comparison of peak intensity in the XRD patterns for the pristine S-LFP/C and TS-LFP/C shown in Figure 3, we found that the ratio of peak intensity is obviously different between the XRD patterns for the two materials, especially for the peaks that matched the (111) and (020) orientations. The discrepancy in the peak ratio may be associated with variation in the atomic positions in the LiFePO$_4$ lattice structure.$^{25,26}$

Figure 5. Ex situ X-ray diffraction (XRD) patterns for the S-LFP/C and TS-LFP/C after 100 cycles at 1 C.

Figure 6. Combined Rietveld refinement of the (a) X-ray powder diffraction and (b) high-resolution powder neutron diffraction patterns for the TS-LFP/C.

Table 2. Lattice Parameters and Atomic Positions of the S-LFP/C and TS-LFP/C Obtained from the Combined Rietveld Refinement Results$^a$

<table>
<thead>
<tr>
<th>atom</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>g</th>
<th>100 × $U_{iso}$/Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>4a</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>1.0</td>
<td>2.28(1)</td>
</tr>
<tr>
<td>Fe</td>
<td>4c</td>
<td>0.2819(1)</td>
<td>0.25</td>
<td>0.9735(2)</td>
<td>1.0</td>
<td>0.89(2)</td>
</tr>
<tr>
<td>P</td>
<td>4c</td>
<td>0.0946(1)</td>
<td>0.25</td>
<td>0.4153(1)</td>
<td>1.0</td>
<td>0.97(1)</td>
</tr>
<tr>
<td>O</td>
<td>4c</td>
<td>0.0971(2)</td>
<td>0.25</td>
<td>0.7438(1)</td>
<td>1.0</td>
<td>1.08(2)</td>
</tr>
<tr>
<td>O</td>
<td>4c</td>
<td>0.4574(1)</td>
<td>0.25</td>
<td>0.2075(2)</td>
<td>1.0</td>
<td>1.69(1)</td>
</tr>
<tr>
<td>O</td>
<td>8d</td>
<td>0.1661(1)</td>
<td>0.0465(1)</td>
<td>0.2864(2)</td>
<td>1.0</td>
<td>1.10(2)</td>
</tr>
</tbody>
</table>

Space group: $Pnma$ (no. 62)

$^{a}$The symbols $g$ and $U_{iso}$ represent the occupation and isotropic thermal parameters, respectively. The numbers in parentheses are the estimated standard deviations of the last significant figure.

Figure 7. Visualization of (a) the LiFePO$_4$ crystal structure and (b) the unit cell structure for the S-LFP/C and TS-LFP/C.

Table 3. Unit Cell and Polyhedral (LiO$_6$, FeO$_6$, and PO$_4$) Volume of the S-LFP/C and TS-LFP/C

<table>
<thead>
<tr>
<th>samples</th>
<th>unit cell volume (Å$^3$)</th>
<th>LiO$_6$ polyhedral volume (Å$^3$)</th>
<th>FeO$_6$ polyhedral volume (Å$^3$)</th>
<th>PO$_4$ polyhedral volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-LFP/C</td>
<td>293.13</td>
<td>12.4968</td>
<td>12.6026</td>
<td>1.8897</td>
</tr>
<tr>
<td>TS-LFP/C</td>
<td>293.09</td>
<td>12.5615</td>
<td>12.6058</td>
<td>1.8688</td>
</tr>
</tbody>
</table>

To examine this phenomenon, combined Rietveld refinements were performed for their XRD and HRPD patterns (Figure 6), and the atomic positions and the lattice parameters evaluated from the refinements are listed in Table 2. In
addition, the LiFePO₄ crystal structure and the unit cell structure for the S-LFP/C and TS-LFP/C are visualized using the refined structural parameters (Table 2) and VESTA program as shown in Figure 7, and the unit cell and polyhedral (LiO₆, FeO₆, and PO₄) volume of the S-LFP/C and TS-LFP/C calculated by the VESTA program is tabulated in Table 3. As a result, the LiO₆ and PO₄ polyhedral volume of the TS-LFP/C are clearly distinguished from those of the S-LFP/C, but there is not much difference in the overall unit cell volume and FeO₆ polyhedral volume between the two materials. The most interesting point here is that the TS-LFP/C with larger LiO₆ polyhedral volume compared with the S-LFP/C is structurally more stable with cycling though the PO₄ polyhedral volume of the TS-LFP/C is smaller than that of the S-LFP/C. In this regard, the minor contraction of the PO₄ polyhedra in the LiFePO₄ crystals may not play a crucial role in determining the structural stability of LiFePO₄. Thus, the presence of the Seed-LFP in the LiFePO₄/C synthesis process enlarges the 1D Li-ion diffusion channel in the resulting LiFePO₄/C, which improves the structural stability of LiFePO₄ after cycling.

4. CONCLUSIONS

In summary, porous and coarse (5−10 μm) LiFePO₄/C composites were synthesized by a simple growth technology using LiFePO₄ nanocrystals as seed crystals for heterogeneous nucleation. In contrast to the LiFePO₄/C prepared by a solution-based process, which was composed of smooth and irregular-shaped LiFePO₄ particles, the LiFePO₄/C obtained by the growth technology showed uniform, porous, and round LiFePO₄ particles, suggesting that the LiFePO₄ seed crystals served as heterogeneous nucleation sites in the 2nd crystallization process. The high initial discharge capacity and superior rate-capability of the LiFePO₄/C prepared by the growth technology was attributed to the high reaction area resulting from the pore tunnels formed inside LiFePO₄ particles and short Li-ion diffusion length. Further, the improved cycling performance of the LiFePO₄/C resulted from the enhanced structural stability against Li-deficient LiFePO₄ phase formation after cycling by the expansion of the 1D Li-ion diffusion channel in the LiFePO₄ crystal structure.

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Notes
The authors declare no competing financial interest.

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