Optimum Morphology of Mixed-Olivine Mesocrystals for a Li-Ion Battery

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ABSTRACT: In this present work, we report on the synthesis of micron-sized LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ (LMFP) mesocrystals via a solvothermal method with varying pH and precursor ratios. The morphologies of resultant LMFP secondary particles are classified into two major classes, flakes and ellipsoids, both of which are featured by the mesocrystalline aggregates where the primary particles constituting LMFP secondary particles are crystallographically aligned. Assessment of the battery performance reveals that the flake-shaped LMFP mesocrystals exhibit a specific capacity and rate capability superior to those of other mesocrystals. The origin of the enhanced electrochemical performance is investigated in terms of primary particle size, pore structure, antisite-defect concentration, and secondary particle shape. It is shown that the shape of the secondary particle has just as much of a significant effect on the battery performance as the crystallite size and antisite defects do. We believe that this work provides a rule of design for electrochemically favorable meso/nanostructures, which is of great potential for improving battery performance by tuning the morphology of particles on multilength scales.

1. INTRODUCTION

Development of advanced lithium-ion batteries that guarantee high energy density, long-term stability, and low cost has been a most important issue due to their versatile use in various devices, such as portable electronics and electric/hybrid vehicles. As for the cathode materials, olivine-structured LiFePO$_4$ has been extensively studied due to its promising properties, including high theoretical capacity, superior safety, long cycle life, and low cost. Even though LiFePO$_4$ cathodes exhibited a low energy density, which results from their relatively low redox potential (3.4 V vs Li$^+$/Li$^0$), continued studies in this field led to a solution with the introduction of Mn. Olivine LiMnPO$_4$ offers a redox potential (4.1 V vs Li$^+$/Li$^0$) higher than that of LiFePO$_4$, providing an energy density higher than that of LiFePO$_4$.

However, previous studies have reported that LiMnPO$_4$ has shown low ionic and electronic conductivity, resulting in poor rate performance and low utilized capacity when used as a cathode. In addition, Mn$^{3+}$ ions formed during electrochemical reactions or materials synthesis are prone to distorting the octahedral environment, lowering its symmetry (Jahn–Teller distortion), in a way that results in the structural instability of the electrode and sluggish kinetics at interfaces during cycling. Such intrinsic drawbacks of LiMnPO$_4$ have been mitigated by replacing Mn atoms with Fe atoms to form a LiMn$_{1-y}$Fe$_y$PO$_4$ solid solution phase. It is now widely accepted that the kinetics of the electrode can be enhanced by utilizing or extending the solid solution phase of LiMn$_{1-y}$Fe$_y$PO$_4$ within certain composition ranges.

With the binary transition-metal phosphate LiMn$_{1-y}$Fe$_y$PO$_4$ being a robust chemistry for realizing superior lithium-ion battery cathodes, various attempts have been made to fabricate the material with electrochemically favorable morphologies. One typical approach is to reduce the particle size down to several tens of nanometers, since nano-sized particles have the benefit of improving the rate performance due to the enhanced conductance by reducing Li$^+$-transport paths and increasing the interfacial area between the electrolyte and active materials. Although the dramatic enhancement of battery performance is expected, nanosizing the material is not yet practical due to the tap density (density of powders after a tapping condensation process, 0.3–0.5 g cm$^{-3}$) being lower than those in commercial cathode materials (>1.0 g cm$^{-3}$), leading to a poor volumetric energy density.

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From this perspective, fabrication of LiMn<sub>1−x</sub>Fe<sub>x</sub>PO<sub>4</sub> with a mesocrystalline structure is an attractive choice among possible alternative morphologies. 31−36 The mesocrystal structure, a superstructure composed of crystallographically oriented nanoparticles, guarantees a high tap density by virtue of the micron-sized secondary particles. 33,34 When it is used for energy storage materials, such a structure is expected to perform well by possessing a high volumetric energy density without compromising Li<sup>+</sup>-diffusion lengths and porosity, which guarantees a large internal surface area and a facile channel for electrolyte infiltration. 34

Numerous groups have successfully tailored various nanostructures of olivine-type transition-metal phosphates based on solvothermal synthesis by controlling the reaction temperature, reaction time, feeding sequence, reducing agents, pH value, solvent, and precursor ratio. 22,40 In spite of such broad interests, successful synthesis of transition-agents, 39 pH value, 22,40 solvent, 25 and precursor ratio. 24,41 In situ X-ray diffraction can provide a direct understanding of the mesocrystalline properties, which are important for applications as energy storage materials. 35,36 The mesocrystalline characteristic of the as-synthesized LiMn<sub>1−x</sub>Fe<sub>x</sub>PO<sub>4</sub> mesocrystals with controlled morphologies has been successfully synthesized by varying the precursor ratio and pH value of the solution in a mixed solvent of N,N-dimethylformamide/water (DMF/H<sub>2</sub>O) and ascorbic acid. The obtained mesocrystals showed high tap densities ranging from 0.86 to 1.23 g cm<sup>−3</sup>. The correlations between meso/nanostructural features (size and shape of secondary/primary particles, porosity, and antisite-defect concentration of an active material) and electrochemical performances were thoroughly examined, and some interesting relations were clearly observed. These outcomes can provide insight into the design of electrochemically favorable structures of an electrode in energy materials.

2. EXPERIMENTAL PROCEDURES

2.1. Materials Preparation. The LiMn<sub>1−x</sub>Fe<sub>x</sub>PO<sub>4</sub> (LMFP) mesocrystals were synthesized by a solvothermal method. First, manganese acetate tetrahydrate (Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, 0.008 M) and iron nitrate nonahydrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 0.002 M) were dissolved in deionized (DI) water (10 mL). The precursor aqueous solution was mixed with N,N-dimethylformamide (DMF) (C,H,N,O, 140 mL) at 80 °C. For the formation of the solid solution of Mn and Fe, the mixed solution was stirred for 1 h at 80 °C and then cooled to room temperature. Subsequently, a varied amount of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and lithium hydroxide monohydrate (LiOH·H<sub>2</sub>O) were introduced into the solution. The molar ratio of LiOH·H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub> was adjusted to 3:1. Afterward, a fixed amount of acetic acid (C<sub>2</sub>H<sub>3</sub>COOH, 0.005 M) was added to the solution. Since the formation of LiMFP is sensitive to the pH value during the solvothermal reaction, a varying amount of nitric acid (HNO<sub>3</sub>, 1.6−3.2 mL) was injected to control the pH of the solution. The mixed solution was transferred to a Teflon-lined autoclave and heated at 180 °C for 12 h. The resulting solution was centrifuged and thoroughly washed with deionized water and acetone, followed by drying at 60 °C overnight. The samples were labeled as LMFP<sub>x</sub>δ<sub>y</sub>(x is the molar ratio of LiOH·H<sub>2</sub>O over the total Mn + Fe source, and y is the amount of HNO<sub>3</sub> added to the solution). For example, LMFP<sub>3.6</sub>1.8 means that the Li/transition metal (TM)/PO<sub>4</sub> molar ratio in the precursor solution was adjusted to 3.6:1:0.1:1.2, and 1.8 mL of HNO<sub>3</sub> was added to the solution (Table S1). The obtained LMFP samples were carbon-coated with the mixed as-synthesized LMFP powders and sucrose dissolved in ethanol (LMFP/sucrose = 7:3 by weight), followed by drying and calcination at 700 °C for 3 h under a H<sub>2</sub>/Ar (4 vol % H<sub>2</sub>) atmosphere.

Chemical delithiation of LMFP was performed by reacting carbon-coated LMFP mesocrystals with nitronium tetrafluoroborate (NO<sub>2</sub>BF<sub>4</sub>) in acetonitrile. First, 500 mg of NO<sub>2</sub>BF<sub>4</sub> was dissolved in acetonitrile (200 mL) with vigorous stirring. Then, 300 mg of the carbon-coated LMFP sample was added to the mixture. The reaction was performed in an argon-filled glovebox, and the resultant was washed with acetonitrile several times to remove any unwanted subproducts.

2.2. Materials Characterization. The crystal structure and grain size of the samples were characterized by X-ray diffraction (XRD, D8 Advance, Bruker). Rietveld refinement of the powder diffraction patterns was conducted with TOPAS (Bruker) software. The morphologies of the samples were observed by field-emission scanning electron microscopy (FESEM, Merlin Compact, Zeiss) and high resolution transmission electron microscopy (HRTEM, JEOL-3500F, JEOL). The pH values of the precursor solution were recorded with a pH meter (CR-10, Denver Instrument). The nitrogen adsorption−desorption isotherms (Micromeritics ASAP 2020) were measured at 77 K, and the specific surface area and pore size distribution of the samples were calculated using the Brunauer−Emmett−Teller (BET) and Barrett−Joyner−Halenda (BJH) methods, respectively. The Fourier-transform infrared (FTIR) spectra (TENSOR27, Bruker) were obtained using KBr pellets, and an elemental analyzer (Flash EA 1112, Thermo Electron Corp.) was employed to determine the relative amount of carbon.

2.3. Electrochemical Measurements. All of the electrochemical performances were carried out using 2016 coin-type half cells with a Li counter electrode. The active materials, super P carbon black, and polyvinylidene fluoride (PVDF) binder were mixed at a weight ratio of 7:2:1. The active materials were spread on an Al current collector with a loading level of ~1 mg cm<sup>−2</sup>. The electrolyte contained 1 M LiPF<sub>6</sub> in ethylene carbonate and diethyl carbonate (EC/DEC = 1/1 vol %) electrolyte. In the case of 0.1 M LiPF<sub>6</sub> electrolyte, 1 M LiPF<sub>6</sub> electrolyte was diluted to one-tenth of its concentration with an EC/DEC solution. The cycling tests were performed in constant current−constant voltage (CC−CV) and a constant current (CC) modes during the charge (delithiation) and discharge (lithiation), respectively. Initially, the electrodes were charged to 4.5 V at a rate of 0.05 C. Once the voltage reached 4.5 V, the current was reduced to a rate of 0.02 C with the 4.5 V fixed voltage and then was further discharged to 2.0 V at various current rates. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses were carried out using a potentiostat (CHI 608C, CH Instrument Inc.). The CV curve was obtained with a scan rate of 10 mV s<sup>−1</sup>, in the voltage range of 2.5−4.7 V. The EIS measurements were carried out by applying a 5 mV harmonic perturbation in the frequency range between 10 mHz and 100 kHz at the open circuit voltage (OCV).

3. RESULTS

3.1. Morphological Features of LMFP Mesocrystals. The X-ray diffraction patterns of selected characteristic samples synthesized at various conditions of different precursor ratios and amounts of HNO<sub>3</sub> are shown in Figure S1. All of the synthesized samples correspond well to the orthorhombic olivine structure with the space group of Pnma, though a small fraction of Li<sub>2</sub>PO<sub>4</sub> seems to be included in samples with relatively higher precursor concentrations (LMFP<sub>3.6</sub>1.7, LMFP<sub>3.6</sub>1.8, and LMFP<sub>3.9</sub>1.8). The residual Li<sub>2</sub>PO<sub>4</sub> may come from the excessive supply of precursor ions and relatively small amount of HNO<sub>3</sub> as Li<sub>2</sub>PO<sub>4</sub> is much less soluble in the high pH range. 22,42,43

The mesocrystalline characteristics (i.e., the existence of crystallographic alignment among the primary particles comprising each secondary particle) and crystallographic
Figure 1. SEM/HREM images and related SAED patterns of (a) LMFP_3.0_1.6, (b) LMFP_3.3_1.8, (c) LMFP_3.6_1.7, (d) LMFP_3.6_1.8, (e) LMFP_3.6_2.9, and (f) LMFP_3.9_1.8.

Figure 2. SEM images of LiMn_{0.8}Fe_{0.2}PO_{4} mesocrystal samples prepared with different precursor ratios (Li/TM/PO_{4}) and various initial pH values.
orientation of the synthesized LMFP samples are identified by SEM and TEM analyses (Figure 1(a–f)). Regardless of the synthetic conditions, all of the resulting particles are of aggregated forms that consist of primary particles. As selected area electron diffraction (SAED) patterns throughout the broad range of all these aggregates exhibit spot patterns instead of ring patterns, it is obvious that the attachments of primary particles are highly oriented. Analysis of the SAED patterns indicates that planes normal to the elongated direction of all the secondary particles are commonly indexed to the (002) plane. In addition, the facets parallel to the shortest dimension (thickness of the flake) of LMFP_3.6_1.8, LMFP_3.6_2.9, and LMFP_3.9_1.8 are composed of (200) facets, as shown in Figure 1. Fast-Fourier-transform (FFT) patterns of selected and overall areas of a representative sample (LMFP_3.6_1.8) indicate that such ordered stacking occurred throughout the secondary particles (Figure S2).

In order to study the effects of precursor ratio and pH variations on the morphology, SEM images of systematically synthesized LMFP mesocrystals were studied and are displayed in Figure 2, and the corresponding morphologies are schematically depicted in Figure 3. Obviously, the morphologies of mesocrystals are dependent on the precursor ratio and pH (amount of HNO₃). As it has been reported that the assemblies of the mesocrystals are the results of complicated interactions among the primary particles, the effects of pH and precursor ratio on the shape and size of the primary particles will be discussed, prior to the overall morphology evolution of the mesocrystals.

From our experiments, the primary particles can be classified as needle- and plate-shaped particles (Figure 3). Namely, the primary particles synthesized with Li/TM/PO₄ ratios of 3.3:1.0:1.1 and 3.0:1.0:1.0 are needle-shaped, whereas the samples synthesized with higher precursor ratios are plate-shaped. Such differentiation of the shape of the nanocrystals is known to be determined by the intermediate phase in dissolution and recrystallization processes. In a solvothermal synthesis, the formation of different intermediate phases can modify the free energy of surfaces of resultant nanocrystals supplying different amounts of ionic species during their dissolution, thus leading to the birth of different-shaped primary particles. The intermediate phases of needle- and plate-shaped primary particles were indexed to be different, which is further discussed.

The average grain size and size distribution of the selected mesocrystals were estimated with SEM images and the Williamson–Hall method by XRD, as shown in Figure S3. The increasing amount of HNO₃ (low pH) results in relatively large primary particles. The smallest primary particles of ~40 nm are observed for samples synthesized from a relatively high pH range of 5–6. The primary particles synthesized in lower pH ranges of 3–5 are slightly larger than those at higher pH ranges (pH 5–6). It can be said that the crystal size is quite sensitive to the H⁺ concentration, where the surfaces of nanocrystals are terminated by H⁺ in the solution and the degree of functionalization determines the critical size of the nanoparticles. Interestingly, particularly large-sized primary particles (~120 nm) are found in LMFP_3.6_2.9, although it was synthesized at the pH value of 3.7 (Figure S3). Such abnormalities are observed in samples synthesized with higher concentrations of Li⁺, PO₄³⁻, and H⁺ (such as LMFP_3.9_2.8 and LMFP_3.9_3.2, as shown in Figure 3). Although the growth mechanisms of these large-sized primary particles are unclear, we consider that these are results from Ostwald ripening after mesocrystal assembly.

Notably, the size of primary particles is generally restricted to 30–50 nm. Such restricted grain growth of primary particles to several tens of nanometers is critical for mesocrystal assembly, and it is attributed to DMF and ascorbic acid (Figures S4–S6). The samples synthesized with less DMF showed particle sizes with broader distributions that were much larger than those of the samples with higher DMF concentrations. Such a correlation between DMF concentration and particle size is indicative of the stabilizing effect of DMF medium (Figure S4). In addition, removal of ascorbic acid seemed to eliminate the ordered attachment between the primary particles. Although the origin of the stabilizing effect of DMF and ascorbic acid is not thoroughly understood through current research, we...
consider that DMF restrains the growth of nanocrystals “electrostatically” by its adhesion on the nanocrystal surfaces. As the assemblies of mesocrystals are known to be the result of the selective adhesions between equivalent planes of primary particles, provided that the particles are stabilized to nano-sized ones, this grain-growth restriction by DMF and ascorbic acid is a prerequisite for mesocrystal formation.

Secondary particles tend to be small when the initial pH value is high (Figure 3). The majority of mesocrystals synthesized at an initial pH value of >6 (such as LMFP_3.3_1.6 and LMFP_3.6_1.7) are found to be smaller than ~1 μm, while the samples with a pH value of <4 (such as LMFP_3.3_3.0 and LMFP_3.6_2.9) are usually larger than ~3 μm. Once again, it is reasonable to say that the growth of the secondary particles occurs through the selective attachment of primary particles, rather than through self-enlargement, since the sum of each primary particle size (30−50 nm) does not seem to fully account for the size growth of the secondary particles. It is more probable that the attachment of primary particles is reinforced as the pH of the solution becomes low.

Secondary aggregates can also be understood by the attachment event of primary particles. As presented in Figure 3, the secondary aggregates can roughly be classified into ellipsoidal- and flake-shaped particles, where the overall shape of the secondary particle is highly dependent on the pH value during synthesis. For instance, LMFP_3.3_1.8, LMFP_3.6_1.7, and LMFP_3.9_1.7 are ellipsoidal, while the slight increase of HNO3 (by 0.1 mL) induced flake-shaped mesocrystals. As mentioned above, the pH of the solution alters the frequency of adhesion onto certain surfaces. It is obvious that when the rate of nanocrystal attachments onto the (200) plane is sufficiently slow, the resulting secondary particles will be the flake-shaped ones, where (200) planes are dominantly exposed compared to the other planes.

Nevertheless, the shape of mesocrystals cannot be explained solely by the initial pH condition of the solution. Since mesocrystal assembly is known to be driven by the dipole moment between primary particles, which is greatly associated with the shape, size, and surface charge of the primary particles, the rate of selective adhesion of each facet can indeed be altered by these factors. The initial shape, size, and surface charge

Figure 4. (a) XRD patterns and (b) SEM images of LMFP_3.6_1.8 samples obtained at different reaction times.
of the primary particles are affected by the Li/TM/PO₄ ratio along with the pH value, and therefore, the overall shape of secondary particles can be affected by varying the precursor ratio of the solvothermal solution.24,40,41,47

The flake-shaped particles are not observed in the synthetic conditions of the first vertical column in Figure 2, where the needle-shaped primary particles are directionally assembled by the dipole moments between the stabilized primary particles. From the TEM and SEM images in Figure 1, it can be seen that the needle-shaped primary particles are elongated to the [001] direction, consistent with the calculation that the surface energies of (010) and (100) in LiMnPO₄ are the lowest and similar to each other.55 Therefore, it can be said that the actual selective adhesion tendency of those two (010) and (100) surfaces can be similar in the needle-shaped primary particles, forming secondary particles that are rounder than the flake-shaped secondary particles. Similarly, flake-shaped secondary particles in the group of LMFP_3.3 (which consists of needle-shaped but less [001]-elongated primary particles) are much more round than ones in the groups of LMFP_3.6 and LMFP_3.9.

Interestingly, mesocrystals formed under the highly acidic conditions have a character such that the primary particles which are placed on an edge of the secondary particles are attached with a slightly tilted form, resulting in dumbbell-shaped mesocrystals.33,38 Such a slightly tilted attachment of primary particles on the original aggregate is known to be caused by the further attachment of primary particles to the already-formed mesocrystals.25,33,55,56 As these dumbbell-shaped particles can be found only in relatively large-sized samples, which are synthesized at lower pH conditions, the

Figure 5. Schematic illustration of the morphological evolution of LiMn₀.₈Fe₀.₂PO₄ mesocrystals.

Figure 6. Charge and discharge profiles of the (a) LMFP_3.0_1.6, (b) LMFP_3.3_1.8, (c) LMFP_3.6_1.7, (d) LMFP_3.6_1.8, (e) LMFP_3.6_2.9, and (f) LMFP_3.9_1.8 samples at various current density rates from 0.05 to 10 C (1 C = 170 mA g⁻¹).
statement can be further validated that the adhesion event of primary particles increases at lower pH conditions.

3.2. Formation Processes of LMFP Mesocrystals. In order to investigate the formation processes of LMFP mesocrystals, we synthesized flake-shaped LMFP-3.6_1.8 samples with different reaction times and analyzed them as shown in Figure 4. Accordingly, the formation mechanisms of the flake-shaped LMFP mesocrystals can be divided into three steps. The first step is the nucleation of Mn/Fe-oxide nanoparticles as a precursor phase, which is confirmed in our previous work.20 In the second step, the formation of flake-like metal phosphate hydrate (M = Fe and Mn) proceeds soon after the introduction of \( \text{H}_2\text{PO}_4 \), LiOH-H\(_2\)O, ascorbic acid, and HNO\(_3\) (denoted as "before solvothermal"). In the third step, once the precursor-based solution is subsequently heated to 180 °C, the plate-like metal–phosphate hydrate particles completely dissolve in 5 min. With the gradual dissolution of the hydrated metal–phosphate phase, the nucleation of LMFP occurs within 30 min (Figure 4(a)). In this stage, the solvothermal reaction produces ~40 nm-sized LMFP nanoparticles. During this period, these primary nanoparticles start to aggregate, reducing the total interfacial free energy of the system along the preferential surface of the LMFP nanoparticles (Figure 4(b)). With an increased reaction time of 1 h, the diffraction intensities of the sample become stronger, indicative of the increased crystallinity and order of the LMFP primary particles (Figure 4(a)).

Likewise, the formation processes of the ellipsoidal-shaped LMFP mesocrystals (LMFP-3.6_1.7) are investigated in a similar way (Figure S7). Consistent with the case of the flake-shaped ones, the initially formed amorphous Mn/Fe-oxide nanoparticles are transformed to the intermediate phase when all of the precursors are added to the solution. Subsequently, after the solution is heated to 180 °C, diffraction peaks of intermediate phases completely disappear in a few minutes, indicating that the phases recrystallize into the final LMFP phase. Notably, the intermediate phase of ellipsoidal-shaped mesocrystals is identified as a metal phosphate hydroxide, which is different from the case of the flake-shaped ones. Schematics of the overall morphological evolution processes of the flake-shaped LMFP mesocrystals are illustrated in Figure 5.

3.3. Electrochemical Performance of LMFP Mesocrystals. The investigation of the battery performance for the LMFP mesocrystals was carried out with selected LMFP samples (LMFP-3.0_1.6, LMFP-3.3_1.8, LMFP-3.6_1.7, LMFP-3.6_1.8, LMFP-3.6_2.9, and LMFP-3.9_1.8) by cycling them at various current densities (sequentially from 0.05 to 10 C) (Figure 6). Prior to the assessment, all six of the selected LMFP samples were carbon-coated to guarantee facile electronic conduction throughout the electrode. As shown in Figure 6, LMFP-3.6_1.8 and LMFP-3.9_1.8 exhibit two discharge plateaus at ~4.1 and ~3.5 V (vs Li+/Li) with a 0.05 C discharge rate, which are related to the redox couple of Mn\(^{3+}/Mn^{2+}\) and Fe\(^{3+}/Fe^{2+}\), respectively. However, in the cases of LMFP-3.0_1.6, LMFP-3.3_1.8, LMFP-3.6_1.7, and LMFP-3.6_2.9, the voltage profiles of the corresponding samples do not show a distinct plateau at 3.5 V, indicating the poor electrochemical reactivity of these electrode materials.

Among the six samples, the flake-shaped LMFP-3.6_1.8 exhibits the highest discharge capacity of ~135 mAh g\(^{-1}\) at 0.05 C (~80% of the theoretical capacity of 170 mAh g\(^{-1}\)). Compared to the LMFP-3.6_1.8 sample, the rest of the samples showed poor discharge capacities (less than ~50% of the theoretical capacity). The rate performance of LMFP-3.6_1.8 is also superior to those of the other samples at all current density rates. At a rate of 10 C, LMFP-3.6_1.8 showed the highest capacity of ~72 mAh g\(^{-1}\) and exhibited the smallest polarization of ~0.5 V compared to those of the other samples. In addition, the cyclic voltammetry (CV) data in Figure S8 also present superior electrochemical kinetics of LMFP-3.6_1.8.

Although the synthetic conditions of the selected samples are slightly different, only LMFP-3.6_1.8 exhibits promising electrochemical performance. Considering the electrochemical properties of LMFP mesocrystals can be stated as a complex function of particle size, morphology, electronic/ionic conduction, antisite defects, etc., we thoroughly examined the origin of the outstanding electrochemical properties for the LMFP-3.6_1.8 electrode.

4. DISCUSSION

In order to elucidate the limiting factors for the electrochemical performance of the LMFP mesocrystals, grain size, P–O vibrational peak position, average pore size, and discharge capacity are plotted in Figure 7 (with the exact values and some additional properties listed in Table 1). It is well-known that...
the electrochemical performance of LMFP particles is significantly affected by particle size. As shown in Figure 7 and Table 1, the grain sizes of the selected LMFP samples are similar to one another (30–60 nm), except for the LMFP_3.6_2.9 sample (~130 nm). Thus, the poor discharge capacity of LMFP_3.6_2.9 can be associated with the larger Li-diffusion length of the sample. However, this does not seem to be the only factor degrading the battery performance of the LMFP mesocrystals, as the electrochemical performances of other similar-sized samples are strikingly different.

The antisite defect, the replacement of a Li atom with a transition-metal atom at its original site (e.g., LiM, where M = Fe or Mn), can also degrade the battery performance by blocking the Li⁺-diffusion channel. During LMFP synthesis, altering the pH, solvent, and precursor concentration can influence the formation of LMFP crystals with different amounts of antisite defects. To estimate the antisite-defect concentration in LiM₀.₆Fe₂O₄ during synthesis, numerous groups have quantified the shifts of P–O symmetric stretching vibrational peaks in FTIR spectra since the P–O bond length is affected by the surrounding MnO₄ and LiO₆ octahedron environment in the olivine structure. From these studies, the red-shift of the peak around ~980 cm⁻¹ is known to reflect the increased antisite-defect concentration in LiM₀.₆Fe₂O₄. As shown in Figure S9, the symmetric stretching peaks of the samples with a higher precursor ratio (samples in LMFP_3.6 or LMFP_3.9 groups) are blue-shifted compared to those of LMFP_3.0_1.6 and LMFP_3.3_1.8 groups. In addition, the low occupancy values at the original Li site in LMFP_3.0_1.6 and LMFP_3.3_1.8, calculated by Rietveld refinement, support the idea that the LMFP mesocrystals synthesized at higher precursor ratios contain fewer antisite defects than those synthesized with lower precursor ratios (Figure S10). The poor electrochemical performances of LMFP_3.0_1.6 and LMFP_3.3_1.8 validate such an assumption. Although it is unreasonable to entirely attribute the inferior capacities of LMFP_3.0_1.6 and LMFP_3.3_1.8 to having a defect concentration higher than those of other samples, the tendency of the red-shift of the vibrational peak around ~980 cm⁻¹ is in line with the resulting discharge capacities among the comparably sized LMFP samples.

The size of primary particles and antisite-defect concentrations still cannot fully explain the gap in the electrochemical performance of the samples. For instance, the discharge capacities of LMFP_3.6_1.7 and LMFP_3.6_1.8 are substantially different, although the two samples possess a similar grain size and antisite-defect concentration. We assume that the reason for the difference in electrochemical performance between LMFP_3.6_1.7 and LMFP_3.6_1.8 is related to the shape of the secondary particles. In Figure 7, a correlation between the average pore size and shape of the mesocrystals, that all the flake-shaped samples showed an average pore size larger than that of the ellipsoidal samples, is observed. As the electrolyte permeation throughout the active material is known to be sluggish when the nanopores are too small, it can be said that the transfer of Li⁺ into the inner grains of the secondary particle can be affected by the shape of the mesocrystals. Also, as shown in the TEM images in Figure 1, the flake-shaped samples display a much lighter contrast than the ellipsoidal samples, indicating that the flake-shaped particles are much thinner and sparser than the ellipsoidal ones. Thus, the ellipsoidal mesocrystals are expected to be too dense and thick to be facilely penetrated by the electrolyte throughout the whole part of the secondary particles, even though the samples show type IV mesoporosity (Figure S11). In addition, ellipsoidal mesocrystals show tap densities (density of powders after a tapping condensation process) higher than those of the similar-sized flake-shaped ones (Table S2). Assuming the size, shape, and internal porosity mainly affect the packing between particles, a different tap density between similar-sized samples can also indicate that the ellipsoidal-shaped mesocrystals are assembled more compactly than the flake-shaped ones.

Assuming that the shape of a mesocrystal affects the permeability of the liquid electrolyte, the rate performances of the flake-shaped LMFP_3.6_1.8 and the ellipsoidal LMFP_3.6_1.7 are assessed utilizing the diluted electrolyte of 0.1 M LiPF₆ (Figures 8 and S12). This experimental condition was designed from the viewpoint that an electrode having a larger effective surface area (actual surface wetted by electrolyte) may experience capacity drop much more severely than one possessing a lower effective surface area when operating at a lower Li⁺ concentration. The LMFP_3.6_1.8 discharged at 0.1 M electrolyte exhibits a capacity of ~135 mAh g⁻¹ at a rate of 0.05 C (8.5 mAh g⁻¹), which is similar to the case using 1 M electrolyte. However, when the samples are discharged with higher current density rates, the discharge capacity of the LMFP_3.6_1.8 tested with diluted electrolyte decreases much more severely than that of the ellipsoidal LMFP_3.6_1.7 (Figure 8). Furthermore, the overpotential of the flake-shaped LMFP_3.6_1.8 significantly increased at the test condition of diluted electrolyte (Figure S12). Compared to that of the flake-shaped LMFP_3.6_1.8, the electrochemical performance of LMFP_3.6_1.7 (ellipsoidal-shaped) with 0.1 M electrolyte is not severely deteriorated from that with 1 M electrolyte, which
indicates that the activation of surface area is very limited in the ellipsoidal-shaped particles (Figure 8).

In addition, experiments comparing the structural behavior toward chemical delithiation of flake-shaped and ellipsoidal-shaped mesocrystals were conducted to show the sluggish Li⁺ penetration into the internal part of the ellipsoidal particles. LMFP_3.6_1.8 (ellipsoidal-shaped) and LMFP_3.6_1.8 (flake-shaped) were selected as the representative samples, and the chemical delithiation of the samples was performed by reacting carbon-coated LMFP mesocrystals with NO₂BF₄ in acetonitrile (Figure S13). These chemically delithiated samples are named D-LMFP_3.6_1.7 (ellipsoidal-shaped) and D-LMFP_3.6_1.8 (flake-shaped). The diffraction peaks of the delithiated metastable phase of LMFP samples are much more prominent in D-LMFP_3.6_1.8 than in D-LMFP_3.6_1.7 (Figure S13). Such results confirm that the flake-shaped MESO-LMFP_3.6_1.8 experiences many more phase transformations by chemical delithiation than D-LMFP_3.6_1.7. Thus, it is reasonable to say that the chemical extraction of Li⁺ via solution from the ellipsoidal samples is much harder than from the flake-shaped samples. The schematic illustration in Figure S14 depicts the morphological effects on the electrolyte permeability of the flake- and ellipsoidal-shaped LMFP mesocrystals.

From the above results, permeation of the electrolyte throughout the active material is shown to be greatly influenced by the shape of a mesocrystal. The optimal electrochemical performance of the flake-shaped LMFP_3.6_1.8 could be obtained since the sample possesses small primary particles, electrochemically favorable morphologies, and a low concentration of antisite defects. Thus, one should take all of these factors into account in order to design electrochemically favorable mesocrystals. Of course, our experiments are limited to flake- and ellipsoidal-shaped mesocrystals, and there can be other morphological factors which may affect the electrochemical performance of a mesocrystal, such as crystal orientation and structural defects. Nevertheless, we believe the observed results can offer a valuable guide for tailoring the electrochemically favorable mesocrystal structures for Li⁺ batteries.

5. CONCLUSIONS

In this work, we have synthesized LiMn₈Fe₀.₂PO₄ (LMFP) mesocrystals exhibiting various morphologies and defect concentrations by controlling the precursor ratios and pH conditions. The resultant morphological evolution of our LMFP mesocrystals upon processing parameters could be understood based upon the nonclassical crystallization theory. The electrochemical performances of the mesocrystals were revealed to be delicately affected by various reaction conditions of the samples. Through fine optimization, the flake-shaped mesocrystals composed of ~40 nm plate-shaped primary particles exhibited optimal electrochemical performance. The origin of this outstanding electrochemical performance was investigated by analyzing the macroscopic-morphological and nanoscopic characteristics. Interestingly, along with the primary particle size and antisite-defect concentration, the shape of the secondary particle was shown to have a significant effect on the battery performance. We believe that this work can provide simple insight into the design of electrochemically favorable meso/nanostructures, which is of great potential for improving the battery performance at the multilength scale.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00501.

Synthetic parameters, notations, and detailed analyses of selected samples; morphologies and phase analyses of samples synthesized with different solvent ratios and reducing atmospheres; and experimental results related to the morphological effects in electrochemical performances (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information

Optimum Morphology of Mixed-Olivine Mesocrystals for Li-Ion Battery

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Table S1. Synthetic parameters of LMFP samples and pH values measured before and after the solvothermal reaction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molar Ratio (Li:TM:PO₄)</th>
<th>Added Amount of HNO₃</th>
<th>Initial pH Value</th>
<th>Final pH Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMFP_3.0_1.6</td>
<td>3.0:1.0:1.0</td>
<td>1.6 ml</td>
<td>5.6</td>
<td>9.0</td>
</tr>
<tr>
<td>LMFP_3.0_1.8</td>
<td>3.0:1.0:1.0</td>
<td>1.8 ml</td>
<td>4.9</td>
<td>8.8</td>
</tr>
<tr>
<td>LMFP_3.0_1.9</td>
<td>3.0:1.0:1.0</td>
<td>1.9 ml</td>
<td>4.8</td>
<td>8.7</td>
</tr>
<tr>
<td>LMFP_3.0_2.0</td>
<td>3.0:1.0:1.0</td>
<td>2.0 ml</td>
<td>3.9</td>
<td>8.3</td>
</tr>
<tr>
<td>LMFP_3.0_2.4</td>
<td>3.0:1.0:1.0</td>
<td>2.4 ml</td>
<td>3.5</td>
<td>8.3</td>
</tr>
<tr>
<td>LMFP_3.3_1.6</td>
<td>3.3:1.0:1.1</td>
<td>1.6 ml</td>
<td>6.1</td>
<td>9.0</td>
</tr>
<tr>
<td>LMFP_3.3_1.8</td>
<td>3.3:1.0:1.1</td>
<td>1.8 ml</td>
<td>5.9</td>
<td>8.9</td>
</tr>
<tr>
<td>LMFP_3.3_2.0</td>
<td>3.3:1.0:1.1</td>
<td>2.0 ml</td>
<td>4.6</td>
<td>8.6</td>
</tr>
<tr>
<td>LMFP_3.3_2.4</td>
<td>3.3:1.0:1.1</td>
<td>2.4 ml</td>
<td>3.8</td>
<td>8.4</td>
</tr>
<tr>
<td>LMFP_3.3_3.0</td>
<td>3.3:1.0:1.1</td>
<td>3.0 ml</td>
<td>3.3</td>
<td>8.2</td>
</tr>
<tr>
<td>LMFP_3.6_1.7</td>
<td>3.6:1.0:1.2</td>
<td>1.7 ml</td>
<td>6.5</td>
<td>9.0</td>
</tr>
<tr>
<td>LMFP_3.6_1.8</td>
<td>3.6:1.0:1.2</td>
<td>1.8 ml</td>
<td>6.1</td>
<td>9.0</td>
</tr>
<tr>
<td>LMFP_3.6_1.9</td>
<td>3.6:1.0:1.2</td>
<td>1.9 ml</td>
<td>5.7</td>
<td>8.9</td>
</tr>
<tr>
<td>LMFP_3.6_2.5</td>
<td>3.6:1.0:1.2</td>
<td>2.5 ml</td>
<td>4.1</td>
<td>8.6</td>
</tr>
<tr>
<td>LMFP_3.6_2.9</td>
<td>3.6:1.0:1.2</td>
<td>2.9 ml</td>
<td>3.7</td>
<td>8.3</td>
</tr>
<tr>
<td>LMFP_3.9_1.7</td>
<td>3.9:1.0:1.3</td>
<td>1.7 ml</td>
<td>6.7</td>
<td>9.1</td>
</tr>
<tr>
<td>LMFP_3.9_1.8</td>
<td>3.9:1.0:1.3</td>
<td>1.8 ml</td>
<td>6.3</td>
<td>8.9</td>
</tr>
<tr>
<td>LMFP_3.9_1.9</td>
<td>3.9:1.0:1.3</td>
<td>1.9 ml</td>
<td>6.1</td>
<td>8.7</td>
</tr>
<tr>
<td>LMFP_3.9_2.8</td>
<td>3.9:1.0:1.3</td>
<td>2.8 ml</td>
<td>3.9</td>
<td>8.3</td>
</tr>
<tr>
<td>LMFP_3.9_3.2</td>
<td>3.9:1.0:1.3</td>
<td>3.2 ml</td>
<td>3.6</td>
<td>8.2</td>
</tr>
</tbody>
</table>
Table S2. Measured tap densities of selected LMFP samples.

<table>
<thead>
<tr>
<th></th>
<th>LMFP 3.0_1.6</th>
<th>LMFP 3.3_1.8</th>
<th>LMFP 3.3_1.7</th>
<th>LMFP 3.6_1.8</th>
<th>LMFP 3.6_2.9</th>
<th>LMFP 3.9_1.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap Density</td>
<td>1.13 g cm(^3)</td>
<td>1.08 g cm(^3)</td>
<td>0.86 g cm(^3)</td>
<td>0.93 g cm(^3)</td>
<td>1.23 g cm(^3)</td>
<td>1.02 g cm(^3)</td>
</tr>
</tbody>
</table>
Figure S1. XRD patterns of the selected LiMn_{0.8}Fe_{0.2}PO_{4} mesocrystal samples.
Figure S2. (a) TEM image of a LiMn_{0.8}Fe_{0.2}PO_4 mesocrystal (LMFP_3.6_1.8) and a selected area electron diffraction pattern of the particle along the [100] zone axis. (b-d) HRTEM images of local areas in the LiMn_{0.8}Fe_{0.2}PO_4 nanoparticles as marked in (a), with the corresponding fast-Fourier-transform (FFT) images along the [100] zone axis.
Figure S3. Primary particle size distribution of LMFP_3.0_1.6, LMFP_3.3_1.8, LMFP_3.6_1.7, LMFP_3.6_1.8, LMFP_3.6_2.9, and LMFP_3.9_1.8 by SEM. The average grain size obtained by SEM was cross-checked with the x-ray diffraction analysis.
**Figure S4.** SEM images of LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ synthesized with different solvent ratios of (a) DMF:H$_2$O = 0.11:1, (b) DMF:H$_2$O = 2:1, and (c) DMF:H$_2$O = 14:1.
Figure S5. XRD patterns of LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ synthesized with different solvent ratios of DMF:H$_2$O = 0.11:1, DMF:H$_2$O = 2:1, and DMF:H$_2$O = 14:1.
Figure S6. (a) XRD patterns and (b) SEM images of LMFP_3.6_1.8 sample synthesized without ascorbic acid.
Figure S7. (a) XRD patterns and (b) SEM images of LMFP_3.6_1.7 samples obtained at different reaction times.
Figure S8. CV curves of (a) LMFP_3.0_1.6, (b) LMFP_3.3_1.8, (c) LMFP_3.6_1.7, (d) LMFP_3.6_1.8, (e) LMFP_3.6_2.9, and (f) LMFP_3.9_1.8 (at the scan rate of 10 mV s^{-1}).
**Figure S9.** FTIR spectra of the selected LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ mesocrystal samples. Peak positions of electrochemically optimized sample (LMFP_3.6_1.8) were marked by dashed lines. Blue and yellow regions correspond to the asymmetric and symmetric stretch modes of PO$_4^{3-}$ tetrahedron, respectively.
Figure S10. Rietveld refinement results of (a) LMFP_3.0_1.6, (b) LMFP_3.3_1.8, (c) LMFP_3.6_1.7, (d) LMFP_3.6_1.8, (e) LMFP_3.6_2.9, and (f) LMFP_3.9_1.8. Occupancy values of atoms at 4a site (original site of Li in LMFP) were calculated for Li and Fe assuming that atomic site changes can occur only between these two atoms. The numbers in parentheses indicate estimated standard deviations of last significant digit.
Figure S11. Nitrogen adsorption-desorption isotherms for the selected LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ mesocrystals, with the pore-size distributions in the inset.
Figure S12. Comparison of the morphological effects of mesocrystals on the electrolyte permeability. The voltage profiles of two different sets of (a) LMFP_3.6_1.8 (flake-shaped), and (b) LMFP_3.6_1.7 (ellipsoidal-shaped), including two half-cell tests, each containing ordinary (1-M LiPF_6) or dilute (0.1-M LiPF_6) concentration of lithium salt.
**Figure S13.** XRD patterns of the carbon coated LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ mesocrystals and their chemically-delithiated samples (D-LMFP).
(a) Ellipsoidal-shaped D-LMFP\_3.6\_1.7 and (b) flake-shaped D-LMFP\_3.6\_1.8.
Figure S14. Schematic illustration of the morphological effects on the electrolyte permeability of the flake- and ellipsoidal-shaped LiMn$_{0.8}$Fe$_{0.2}$PO$_4$ mesocrystals.