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Synthesis of LiMn_{0.75}Fe_{0.25}PO_{4}/C microspheres using a microwave-assisted process with a complexing agent for high-rate lithium ion batteries

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LiMn_{0.75}Fe_{0.25}PO_{4}/C microspheres were synthesized using a microwave-assisted process with a complexing agent. In this process, it was found that the various states of the complexing agent for different pH of the precursor solution have significant effects on the obtained micro spherical morphology. Furthermore, the concentration of antisite defects in the samples was also found to be affected by the pH of the precursor. The prepared secondary spheres have a high tap density of 1.3 g cm\textsuperscript{-3} and deliver a reversible capacity of 163 mAh g\textsuperscript{-1} at a 0.05 C-rate. Furthermore, remarkable rate capability is obtained, with 57% capacity retention at a 60 C-rate, as well as excellent cyclability, with 99.3% capacity retention after 100 cycles at 1 C-rate.

Introduction

Olivine-structured LiFePO\textsubscript{4} has been considered a promising cathode material for lithium ion batteries (LIBs) because of its low cost, high theoretical capacity, environmental friendliness, and thermal stability.\textsuperscript{1, 2} However, LiFePO\textsubscript{4} has a lower energy density than conventional cathode materials because of its low operation voltage (3.5 V vs. Li/Li\textsuperscript{+}). Therefore, LiMnPO\textsubscript{4}, which has a higher operation voltage (4.1 V vs. Li/Li\textsuperscript{+}), is currently considered a more appropriate cathode material than LiFePO\textsubscript{4}.\textsuperscript{3-6} Up to now, the use of LiMnPO\textsubscript{4} in electrochemical applications has been limited by its extremely poor electronic conductivity (<10\textsuperscript{-12} S cm\textsuperscript{-1}), low lithium diffusion rate (<10\textsuperscript{-10}-10\textsuperscript{-14} cm\textsuperscript{2} s\textsuperscript{-1}), Jahn-Teller distortion during the charge-discharge process, and unstable delithiated phase.\textsuperscript{7-12} Among these problems, a key factor preventing more widespread utilization of LiMnPO\textsubscript{4} is its very low Li\textsuperscript{+} diffusion rate at the mismatched MnPO\textsubscript{4}-LiMnPO\textsubscript{4} interface.\textsuperscript{8}

In order to resolve these problems with LiMnPO\textsubscript{4}, the Fe-doped LiMn\textsubscript{1-x}Fe\textsubscript{x}PO\textsubscript{4} solid solution system has been suggested.\textsuperscript{6, 7, 13-16} Previous research on LiMn\textsubscript{1-x}Fe\textsubscript{x}PO\textsubscript{4} has focused on the synthesis of nanoparticles to improve the Li\textsuperscript{+} diffusion in the LiMn\textsubscript{1-x}Fe\textsubscript{x}PO\textsubscript{4} solid solution system. This approach has led to good cell performance, including high specific capacitance and rate capabilities.\textsuperscript{6, 17-19} However, the nanoparticles have a low tap density, which limits the volumetric energy density.\textsuperscript{20, 21} For example, nanoparticles have tap densities of 0.3–0.8 g cm\textsuperscript{-3}, whereas the conventional oxide electrode material LiCoO\textsubscript{2} has a tap density of 2.6 g cm\textsuperscript{-3}. In addition, the extended contact area between the nanoparticles and the electrolyte leads to undesirable side reactions, poor thermal stability, and poor cycling stability.\textsuperscript{21}

In contrast with nanoparticles, LiMn\textsubscript{1-x}Fe\textsubscript{x}PO\textsubscript{4} microspheres composed of nanosized primary particles can provide a high tap density, high volumetric energy density, and good cyclability. A few studies have focused on the synthesis of microspheres to improve the tap density and electrochemical properties of the material.\textsuperscript{22-27} Sun et al. used a co-precipitation technique to fabricate LiMn\textsubscript{0.85}Fe\textsubscript{0.15}PO\textsubscript{4}/C microspheres with a high volumetric capacity.\textsuperscript{24} Liu et al. used a spray-drying technique to fabricate LiMn\textsubscript{0.6}Fe\textsubscript{0.4}PO\textsubscript{4}/C microspheres with a high specific capacity and good rate capability.\textsuperscript{26} However, the previously reported methods have been time-consuming, complex two-step or multistep processes involving the use of a microsized spherical MPO\textsubscript{4}•H\textsubscript{2}O (M=Fe, Mn) precursor or spray-drying of presynthesized nanoparticles. In addition, microsized LiMn\textsubscript{1-x}Fe\textsubscript{x}PO\textsubscript{4} particles have limited specific capacitance and rate capability, since their Li\textsuperscript{+} diffusion path is longer than that of the nanoparticles, which leads to electrochemical isolation of the inner parts of the particles.\textsuperscript{23} Therefore, a simple and facile synthesis of micro spherical LiMn\textsubscript{1-x}Fe\textsubscript{x}PO\textsubscript{4} particles with a high tap density and superior rate capability is highly desirable.

Herein, we report a microwave-assisted synthesis of LiMn\textsubscript{1-x}Fe\textsubscript{x}PO\textsubscript{4}/C (x = 0.25) microspheres with a complexing agent to achieve both a high tap density and superior rate capability. In particular, we control the pH of the precursor solution to fabricate LiMn\textsubscript{0.75}Fe\textsubscript{0.25}PO\textsubscript{4}/C secondary spheres with a high tap density and low concentration of antisite defects.
morphology and structure of obtained microspheres were characterized by means of field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) analysis. The antisite defect concentration was analyzed by performing Fourier transform infrared spectroscopy (FTIR) measurements. Finally, it is found that the LiMn_{1-x}Fe_{x}PO_4 microspheres prepared in this study exhibit a high tap density, high specific capacity, excellent rate performance, and superior cycling stability as cathode materials for LIBs.

Experimental

Materials synthesis

The LiMn_{0.75}Fe_{0.25}PO_4 microspheres were synthesized with a complexing agent using a simple and facile microwave-assisted process. To fabricate LiMn_{1-x}Fe_{x}PO_4 microspheres with low concentrations of antisite defects, the pH of the precursor was controlled by using a mixed P source consisting of H_3PO_4 (Aldrich) and (NH_4)H_2PO_4 (Aldrich). The LiOH · H_2O (Aldrich) aqueous solution (1.5 M) and xH_3PO_4 + (1-x)(NH_4)H_2PO_4 (0 ≤ x ≤ 1) aqueous solution (0.5 M) were mixed with sucrose in a weight ratio of 9:1. The mixture was then sintered at 650 °C for 3 hours under an Ar/H_2 (95/5) mixture was rapidly heated to 200 °C at a power of 200 W. During the synthesis, the solution temperature was maintained at 200 °C for 15 min with rotation and magnetic stirring. After the reaction, the vessel was cooled down to room temperature, and the final product was repeatedly washed with distilled water and acetone by centrifugation and then dried at 60 °C for 6 h in a convection oven. To provide a uniform carbon coating on the surfaces of the LiMn_{0.75}Fe_{0.25}PO_4 microspheres, they were mixed with sucrose in a weight ratio of 9:1. The mixture was then sintered at 650 °C for 3 hours under an Ar/H_2 (95/5 vol%) atmosphere with a heating rate of 5 °C min^{-1}.

Materials characterization

The crystalline phase of the samples was characterized by performing powder XRD (Dmax 2200, Rigaku) measurements with Cu-Kα radiation (λ = 1.5406 Å). The morphologies of the samples were observed by performing FE-SEM (JSM-7001F, JEOL Ltd.), TEM (CM 200, Philips), and high resolution TEM (HRTEM, JEM 2100F, JEOL Ltd.). The cross-sectional TEM specimens were prepared by slicing microspherical LiMn_{0.75}Fe_{0.25}PO_4/C particles embedded in an epoxy resin with an ultramicrotome (UMT, MTX ultramicrotome, Tucson). The nitrogen adsorption-desorption isotherms (Autosorb-iQ 2ST/MP, Quantachrome) were measured at 77 K, and the surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The pH values of the precursor and of the solution remaining after the end of reaction were recorded using a pH meter (Orion 3-star Benchtop Meter, Thermo Scientific). FTIR spectra (Vertex 70, Bruker) were obtained using KBr pellets. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis (OPTIMA 7300DV, Perkin Elmer) was carried out to investigate the chemical composition of the LiMn_{0.75}Fe_{0.25}PO_4/C powders. An elemental analyzer (2400 Series II CHNS/O, Perkin Elmer) was employed to determine the amount of carbon in the final products.

Electrochemical measurements

The working electrode was prepared by mixing 70 wt.% LiMn_{0.75}Fe_{0.25}PO_4/C microspheres, 20 wt.% acetylene black, and 10 wt.% polyvinylidene fluoride (PVDF; Aldrich) dissolved in N-methylpyrrolidone (NMP; Aldrich) as a binder. The slurry was coated on aluminum foil and dried in a vacuum oven at 100 °C for 24 h. The electrode was pressed with a rolpress machine. Each working electrode had an area of 1.13 cm^2 and the amount of active material in the electrode was 2 ~ 3 mg/cm^2. The electrochemical properties were investigated using CR2032 coin cells with lithium metal as the counter electrode. The electrolyte was 1 M LiPF_6 dissolved in a mixture of ethylene carbonate (EC)-ethyl methyl carbonate (EMC)-diethyl carbonate (DEC) at a volume ratio of 3:5:2. Cyclic voltammetry and galvanostatic charge/discharge tests were carried out between 2.0 and 4.5 V (vs. Li/Li^+) using a potentiostat/galvanostat (MPG2, Bio-Logic).

Results and discussion

Fig. 1a shows the XRD pattern of the LiMn_{0.75}Fe_{0.25}PO_4/C microspheres. All diffraction peaks of the LiMn_{0.75}Fe_{0.25}PO_4/C microspheres prepared at pH 6.35 correspond to those of orthorhombic olivine-structured materials with the Pnma space group (JCPDS card No. 74-0375). Possible impurities such as lithium phosphate or metal phosphate were not detected in the XRD pattern, reflecting the high purity of the prepared sample. All diffraction peaks of LiMn_{0.75}Fe_{0.25}PO_4/C are significantly shifted to the right relative to those of phase-pure LiMn_{0.75}Fe_{0.25}PO_4. From the XRD data, the lattice constants of LiMn_{0.75}Fe_{0.25}PO_4/C microspheres were calculated to be a = 10.42 Å, b = 6.08 Å, c = 4.73 Å, and V = 299.70 Å^3, which are in good agreement with the lattice constants reported for phase-pure LiMn_{0.75}Fe_{0.25}PO_4. This means that the obtained LiMn_{0.75}Fe_{0.25}PO_4/C microspheres were a solid solution of LiMnPO_4 and LiFePO_4. Fig. 1b shows FE-SEM image of the LiMn_{0.75}Fe_{0.25}PO_4/C microspheres. It can be seen that the LiMn_{0.75}Fe_{0.25}PO_4/C microspheres are composed of smaller primary particles with sizes of about 100 nm. The sizes of microspheres were uniform at about 2–3 μm. It is well known that a microspherical...
morphology can help improve the tap density of the powder, because microspherical powders can be packed well.24, 26 In fact, the LiMn0.75Fe0.25PO4/C microspheres have a high tap density of 1.3 g cm−3, which is higher than the typical tap densities of nanoparticles of 0.3–0.8 g cm−3. The high tap density of the microsized secondary particles helps to improve the volumetric capacity.21 The EDS elemental mapping results for the LiMn0.75Fe0.25PO4/C microspheres are shown in Fig. S1. The Fe, Mn, C, P, and O species were uniformly distributed in the microspherical particles, and it is clear that the carbon was uniformly coated on the surfaces of the LiMn0.75Fe0.25PO4/C microspheres.

Fig. 1c shows a cross-sectional TEM image of a LiMn0.75Fe0.25PO4/C microsphere. It can be seen that the LiMn0.75Fe0.25PO4/C microspheres have a porous structure consisting of primary 50–100 nm nanoparticles and nanopores with diameters less than 50 nm. The nanosized primary particles create a network of nanopores that acts as a continuous pathway for the electrolyte ions to enter into the microsized materials, resulting in enhanced accessibility for Li ions throughout the structure. Fig. 1d shows an HR-TEM image of a LiMn0.75Fe0.25PO4/C microsphere. The HR-TEM image clearly shows a well-crystallized structure with lattice fringes of ca. 0.42 nm corresponding to the (101) interplanar spacing of the LiMn0.75Fe0.25PO4.6, 18 The thickness of the amorphous carbon layer on the surface of the LiMn0.75Fe0.25PO4/C microspheres was approximately 1.5–2 nm. The carbon content of the LiMn0.75Fe0.25PO4/C microspheres was measured to be 3 wt.% by elemental analysis (not shown here). The uniform and thin carbon coating improves the electrochemical performance of the LiMn0.75Fe0.25PO4/C microspheres.28

Fig. 2 shows the nitrogen adsorption-desorption isotherms and the corresponding Barrett-Joyner-Halenda (BJH) pore-size distribution curve of the LiMn0.75Fe0.25PO4/C microspheres. It can be seen that the LiMn0.75Fe0.25PO4/C microspheres exhibit a typical type IV isotherm with a type H2 hysteresis loop, indicating a mesoporous structure. The specific surface area of the LiMn0.75Fe0.25PO4/C microspheres was 23.2 m2 g−1, which confirms the porous structure. As shown in Fig. 2 (b), the mean pore size of the LiMn0.75Fe0.25PO4/C microspheres was 3.8 nm, and the distributions showed a uniform pore size with a sharp peak. The corresponding cumulative desorption volume of the pores is 0.06 cm3 g−1. These results support the conclusions about the porous structure derived from Fig. 1c above.

In order to investigate the mechanism for the formation of the micro spherical LiMn0.75Fe0.25PO4/C particles, experiments were carefully carried out with different pH values of the precursor solution. Fig. 3 shows FE-SEM images of the samples prepared with precursors with different pH. The samples denoted as LMFP1, LMFP2, LMFP3, and LMFP4 were obtained from precursors with pH values of 5.74, 6.01, 6.35, and 7.89, respectively. As shown in Fig. 3a, LMFP1 has
an irregular morphology consisting of agglomerated nanoparticles. The LMFP2 shown in Fig. 3b are more spherical than the LMFP1. When the pH is increased to 6.35 and above, a surprising morphological change can be observed: LMFP3 and LMFP4 exhibit perfectly spherical morphologies, as shown in Fig. 3c and Fig. 3d. These spherical secondary particles are monodisperse, with a uniform size of about 2–3 μm. Thus, more microspherical morphologies were obtained in this synthesis system with increasing pH of the precursor, and we conclude that the pH of the precursor is a key factor affecting the resultant LiMn_{0.75}Fe_{0.25}PO_{4/C} microspheres. Furthermore, time-dependent experiments at a fixed precursor pH of 6.35 proved that a more microspherical morphology is formed as time progresses in the microwave-assisted process, as shown in Fig. S2. To further gain insight into the effects of temperature on the formation of microspherical particles, different synthesis temperatures were used at a fixed precursor pH of 6.35. As shown in Fig. S3, the reaction temperature has no significant effect on the morphology of the product.

Based on the above experimental results, a possible mechanism for the formation of LiMn_{0.75}Fe_{0.25}PO_{4/C} microspheres is proposed, as schematically illustrated in Fig. 4. It is well-known that the complexing agent acts as templates for synthesis of microspherical particles. In aqueous solution, citric acid has different properties depending on the pH. In particular, the pH has a critical role in deciding the oxidation state of the citrate ions C_{6}H_{8}O_{7}^{−}: at low pH, the citric acid is not fully ionized and forms [C_{4}H_{2}O_{7}] or [C_{4}H_{2}O_{7}^{2−}], whereas at high pH, [C_{6}H_{8}O_{7}^{−}] is mostly formed as a result of full ionization. Therefore, when the pH of the precursor is increased, the electrostatic interactions between the citrate ions and metal ions are increased. At high pH, after the metal ion is uniformly bonded to [C_{6}H_{8}O_{7}^{−}], the LiMn_{0.75}Fe_{0.25}PO_{4} precursor nuclei form homogeneously on all chelation sites on the citrate ions. These nuclei grow at the expense of smaller ones, following the Ostwald ripening process. Then, the primary nanoparticles begin to assemble together to minimize the surface free energy of the system. Because citrate ions can form hydrogen bonds to each other, the primary particles grown from nuclei that were originally homogeneously distributed on the chelation sites of citrate ions at high pH can easily aggregate into microspherical secondary particles to minimize the surface energy. Thus, uniform microspherical secondary particles are fabricated at high pH, because of the uniform distribution of the nuclei on the chelation sites of the citrate ions and the interactions between citrate ions. In contrast, at low pH, free metal ions exist in the solution, because the citric acid is not fully ionized. In this case, nuclei form randomly and are only partially bonded to citrate ions. As a result, self-assembly leads to secondary particles with irregular morphologies because of the weak interactions between the citrate ions and metal ions. Thus, whether LiMn_{0.75}Fe_{0.25}PO_{4/C} microspheres form depends on the state of the citric acid at the chosen pH of the precursor.
Fig. 5 (a) XRD patterns and (b) FT-IR spectra of LiMn_{0.75}Fe_{0.25}PO_4/C prepared from precursors with different pH.

Table 1 Atomic ratios determined by ICP-OES analysis of LiMn_{0.75}Fe_{0.25}PO_4/C prepared from precursors with different pH.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Li/P</th>
<th>Mn/P</th>
<th>Fe/P</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMFP1</td>
<td>0.90</td>
<td>0.74</td>
<td>0.26</td>
</tr>
<tr>
<td>LMFP2</td>
<td>0.97</td>
<td>0.74</td>
<td>0.26</td>
</tr>
<tr>
<td>LMFP3</td>
<td>1.00</td>
<td>0.75</td>
<td>0.25</td>
</tr>
<tr>
<td>LMFP4</td>
<td>1.03</td>
<td>0.73</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Fig. 5a shows the XRD patterns of the LiMn_{0.75}Fe_{0.25}PO_4/C samples prepared at different pH. LMFP1, LMFP2, and LMFP3 (with precursor pH ≤ 6.35) maintained a single-phase olivine structure (ICPDS card No. 74-0375). In the XRD pattern of LMFP4 (precursor pH = 7.89), small Li_2PO_4 peaks appeared at 23.2°, 24.8°, 33.8°, and 36.8°. It has been reported that Li_2PO_4 is generated at high pH because the solubility of Li_3PO_4 in basic solutions is very low.

The FTIR spectra in this range are widely used to determine the antisite defect concentrations in olivine-structured materials. The FTIR spectra of the synthesized LiMn_{0.75}Fe_{0.25}PO_4/C show the typical bands of olivine-structured materials reported elsewhere. The vibration modes corresponding to the bands above 400 cm^{-1} are known to be external modes associated with the intramolecular vibrations of the PO_4 and MnO_6/FeO_6 units. The bands in the range of 500–580 cm^{-1} are known to correspond to the (ν_3 + ν_2) bending modes of (PO_4)^3-, and the band in the vicinity of 460 cm^{-1} is assumed to be a (ν_2 + ν_3) mode of (PO_4)^3- involving lithium-ion motion. The band near ν_3 = 980 cm^{-1} is identified as the symmetric stretching mode. Bands related to the antisymmetric stretching mode of the P-O bond (ν_3) appear in the region of 1070–1139 cm^{-1}. The bands near 636 cm^{-1} are known to be bending modes of MnO_6/FeO_6 octahedrons.

In olivine-structured materials, the antisite defect is a defect in which a transition metal resides in the lithium site in the crystal lattice. Olivine-structured materials synthesized using the hydrothermal method intrinsically form M_{Li} (M = Mn, Fe) antisite defects. These intrinsic antisite defects block the Li^+ migration channel and greatly degrade the electrochemical performance. As shown in Fig. 5b, the absorption band around 980 cm^{-1} of the samples shifts from 995 to 983 cm^{-1} with increasing precursor pH. This peak shift is related to a change in the antisite defect concentration.

To verify the chemical formula of the LiMn_{0.75}Fe_{0.25}PO_4/C, the Li/P, Mn/P, and Fe/P atomic ratios of each sample were measured by ICP-OES analysis, as shown in Table 1. The Mn/P and Fe/P atomic ratios were similar for all samples, in the ranges of 0.73–0.75 and 0.24–0.27, respectively. However, the Li/P atomic ratio increased from 0.90 to 1.03 with increasing precursor pH. The Li/P atomic ratios for LMFP1, LMFP2, and LMFP3 gradually increased to 1. These results are consistent with the FTIR spectra in suggesting that the concentration of M_{Li} (M = Mn, Fe) antisite defects decreases with increasing precursor pH. As mentioned above, the Li/P atomic ratios (Mn/P + Fe/P) for LMFP3 were close to 1, which is thought to be obtained near the equilibrium state, and LMFP3 showed a single-phase olivine structure without any impurities. In contrast, the Li/P atomic ratio for LMFP4 was significantly higher because it contains Li_2PO_4 impurities. Finally, ICP-OES analysis of the products revealed that the Li/P, Mn/P, and Fe/P...
The charge-discharge curves of LMFP3 at 0.05 C-rate measured at 25 °C are shown in Fig. 5. The charge and discharge capacities of LMFP3 were found to be 168 mAh g⁻¹ and 163 mAh g⁻¹ at 0.05 C-rate, respectively, which corresponds to 95.3% of the theoretical capacity. The coulombic efficiency (calculated from the discharge capacity/charge capacity) was about 97%. In addition, the discharge capacity in terms of the volumetric capacity at 0.05 C-rate is 262 mAh cm⁻³, which is similar to the reported value.⁶ The charge and discharge tests were performed at the same C-rates. The discharge capacity measured at the extremely high 60 C-rate was about 100 mAh g⁻¹, which is 57% of the specific capacity at 0.05 C-rate, indicating the excellent high-rate capability of the prepared LiMn₀.₇₅Fe₀.₂₅PO₄/C microspheres (Fig. 6c). This could be attributed to the uniform carbon coating on the surface of LiMn₀.₇₅Fe₀.₂₅PO₄/C microspheres, which effectively reduced the charge transfer resistance. Furthermore, the porous spherical structure of the LiMn₀.₇₅Fe₀.₂₅PO₄/C microspheres ensures deep penetration of the electrolyte into inner parts of micro spherical secondary particles, enabling full electrophysical utilization of the LiMn₀.₇₅Fe₀.₂₅PO₄/C microspheres.

Fig. 6d shows the cycling stability of LMFP3. The cycling test was conducted at 25 °C for 100 cycles at a charge/discharge rate of 1 C-rate. The initial discharge capacity was 152 mAh g⁻¹. After 100 cycles, LMFP3 delivered a discharge capacity of 151 mAh g⁻¹, which corresponds to 99.3% capacity retention. In addition, the coulombic efficiency remained at about 96%, demonstrating the excellent cyclability of LMFP3. This indicates the excellent structural stability of LMFP3 during repeated cycling.

Conclusion
In summary, LiMn₀.₇₅Fe₀.₂₅PO₄/C microspheres were synthesized using a facile and simple microwave-assisted process with a complexing agent. It was found that the different states of the complexing agent for different pH of the precursor solution have significant effects on the obtained microspherical morphology and the electrophysical performance. The obtained microspherical secondary particles were composed of nanosized primary particles. The LiMn₀.₇₅Fe₀.₂₅PO₄/C microspheres exhibited a high tap density of 1.3 g cm⁻³, a reversible capacity of 163 mAh g⁻¹ at a 0.05 C-rate, and remarkable rate capability, with 57% capacity retention at a 60 C-rate. In addition, excellent cyclability was observed, with 99.3% capacity retention after 100 cycles at 1 C-rate. These superior properties could be attributed to the porous spherical structure, uniform carbon coating layer, and the reduction of the antiseite defect concentration.
Acknowledgements
This work was supported by the energy efficiency and resources of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Ministry of Knowledge Economy, Korean government (No: 20122010100140), and also supported by POSCO.

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Synthesis of \( \text{LiMn}_{0.75}\text{Fe}_{0.25}\text{PO}_4/C \) microspheres using a microwave-assisted process with a complexing agent for high-rate lithium ion batteries

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LiMn$_{0.75}$Fe$_{0.25}$PO$_4$/C microspheres were synthesized using a microwave-assisted process with a complexing agent through the control of precursor pH. The prepared secondary spheres have a high tap density of 1.3 g cm$^{-3}$ and deliver a reversible capacity of 163 mAh g$^{-1}$ at a 0.05 C-rate. Furthermore, remarkable rate capability is obtained, with 57% capacity retention at a 60 C-rate, as well as excellent cyclability, with 99.3% capacity retention after 100 cycles at 1 C-rate. These superior properties could be attributed to the porous spherical structure, uniform carbon coating layer, and the reduction of the antisite defect concentration.