Supporting Information

Rational design of synthetic strategy, carburizing approach and pore-forming pattern to unlock cycle reversibility and rate capability of micro-agglomerated LiMn_{0.8}Fe_{0.2}PO_4 cathode materials

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Synthesis of LMFP-3S1C: Stoichiometric amounts of 0.01 mol Li_2CO_3, 0.016 mol MnC_2O_4\cdot2H_2O, 0.004 mol FeC_2O_4\cdot2H_2O and 0.02 mol NH_4H_2PO_4 were mixed thoroughly with sucrose (1.65g). The mixture was dissolved in acetone and ball-milled for 10h using a zirconia milling media. Then, the mixture was dried, ground and presintered at 350°C for 5 h (at a heating rate of 2 °C min^{-1}) under a flow of N_2/H_2 (partial pressure ratio: 95/5) atmosphere to pyrolyze the blend raw materials. After an identical pretreatment, the second calcination was first carried out at 220°C (heating rate of 2°C min^{-1}) for 3 h to precondense the inorganic precursor, then heated at the same rate to 450°C and remain for 5h under the same atmosphere conditions. Finally, after an identical pretreatment again, the third calcination temperature was raised to 600°C under the same heating condition as second stage and remained for 10h.

Synthesis of LMFP-3S3C: Stoichiometric amounts of 0.01 mol Li_2CO_3, 0.016 mol MnC_2O_4\cdot2H_2O, 0.004 mol FeC_2O_4\cdot2H_2O and 0.02 mol NH_4H_2PO_4 were mixed thoroughly with sucrose (0.55g). The mixture was dissolved in acetone and ball-milled for 10h using a zirconia milling media. Then, the mixture was dried, ground and presintered at 350°C for 5 h (at a heating rate of 2 °C min^{-1}) under a flow of N_2/H_2 (partial pressure ratio: 95/5) atmosphere to pyrolyze the blend raw materials. At the second stage, the precursor was remixed with 0.55g sucrose. After an identical
pretreatment, the calcination was first carried out at 220°C (heating rate of 2°C min⁻¹) for 3 h to precondense the inorganic precursor, then heated at the same rate to 450°C and remain for 5h under the same atmosphere conditions. Finally, after a reintroduction of 0.55g sucrose and an identical pretreatment, the third calcination temperature was raised to 600°C under the same heating condition as second stage and remained for 10h.

Fig. S1 Schematic view of procedure for preparing (a) LMFP-3S1C and (b) LMFP-3S3C cathode materials.

Fig. S2 TGA curves of LMFP-3S1C, LMFP-3S3C and LMFP-3S3C2P.
Fig. S3 (a) X-ray diffraction patterns at different heat-treatment temperatures during pristine LMFP synthesis via a three-step solid-state reaction, and (b) crystal lattice parameters of LMFP-3S1C, LMFP-3S3C and LMFP-3S3C2P composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>V(Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMFP-3S1C</td>
<td>10.4098(8)</td>
<td>6.0707(6)</td>
<td>4.7288(7)</td>
<td>298.85(5)</td>
</tr>
<tr>
<td>LMFP-3S3C</td>
<td>10.4111(7)</td>
<td>6.0733(4)</td>
<td>4.7267(2)</td>
<td>298.87(3)</td>
</tr>
<tr>
<td>LMFP-3S3C2P</td>
<td>10.4046(2)</td>
<td>6.0674(4)</td>
<td>4.7311(3)</td>
<td>298.67(3)</td>
</tr>
</tbody>
</table>

Fig. S4 Typical TEM images and the corresponding FFT spots (inset) for a single LMFP-3S1C primary particle.
Fig. S5 (a) TEM images of LMFP-3S3C and (b) typical TEM images and the corresponding FFT spots (inset) for LMFP-3S3C composites containing several primary particles.

Fig. S6 Cross-sectional SEM images of the prepared (a) LMFP-3S1C, (b) LMFP-3S3C and (c) LMFP-3S3C2P electrodes.
Fig. S7 Comparison of volumetric capacity at various rates from 0.1 C to 20 C for LMFP-3S1C, LMFP-3S3C and LMFP-3S3C2P composites.