## Supporting Information

Rational design of synthetic strategy, carburizing approach and poreforming pattern to unlock cycle reversibility and rate capability of micro-agglomerated LiMn<sub>0.8</sub>Fe<sub>0.2</sub>PO<sub>4</sub> cathode materials Yan Wang,<sup>ab</sup> Cheng-Yu Wu,<sup>a</sup> Hao Yang,<sup>a</sup> and Jeng-Gong Duh<sup>\*a</sup>

 <sup>a</sup> Department of Material Science and Engineering, National Tsing-Hua University, Hsinchu, Taiwan
\*Corresponding author e-mail: jgd@mx.nthu.edu.tw
<sup>b</sup> School of Chemical Engineering & Pharmacy, Wuhan Institute of Technology, Wuhan 430074, China

Synthesis of LMFP-3S1C: Stoichiometric amounts of 0.01 mol Li<sub>2</sub>CO<sub>3</sub>, 0.016 mol  $MnC_2O_4 \cdot 2H_2O$ , 0.004mol FeC<sub>2</sub>O<sub>4</sub>  $\cdot 2H_2O$  and 0.02 mol NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> 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<sup>-1</sup>) under a flow of N<sub>2</sub>/H<sub>2</sub> (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<sup>-1</sup>) 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<sub>2</sub>CO<sub>3</sub>, 0.016 mol MnC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O, 0.004mol FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O and 0.02 mol NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> 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<sup>-1</sup>) under a flow of N<sub>2</sub>/H<sub>2</sub> (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<sup>-1</sup>) 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.



**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.