Electronic Supplementary Information (ESI)

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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Supplementary Table

Table. S1 Compositions of the precursor solutions for synthesis of microspherical $LiMn_{0.75}Fe_{0.25}PO_4/C$. The pH values of the solutions were measured before and after the reaction.

Sample	H_3PO_4 / mmol	$(NH_4)H_2PO_4$ / mmol	LiOH/ mmol	$MnSO_4$ / mmol	$FeSO_4$ / mmol	pH (precursor)	pH (product)
LMFP1	6	0	18	4.5	1.5	5.74	4.49
LMFP2	4.5	1.5	18	4.5	1.5	6.01	5.37
LMFP3	1.5	4.5	18	4.5	1.5	6.35	6.02
LMFP4	0	6	18	4.5	1.5	7.89	6.95

Supplementary Figures

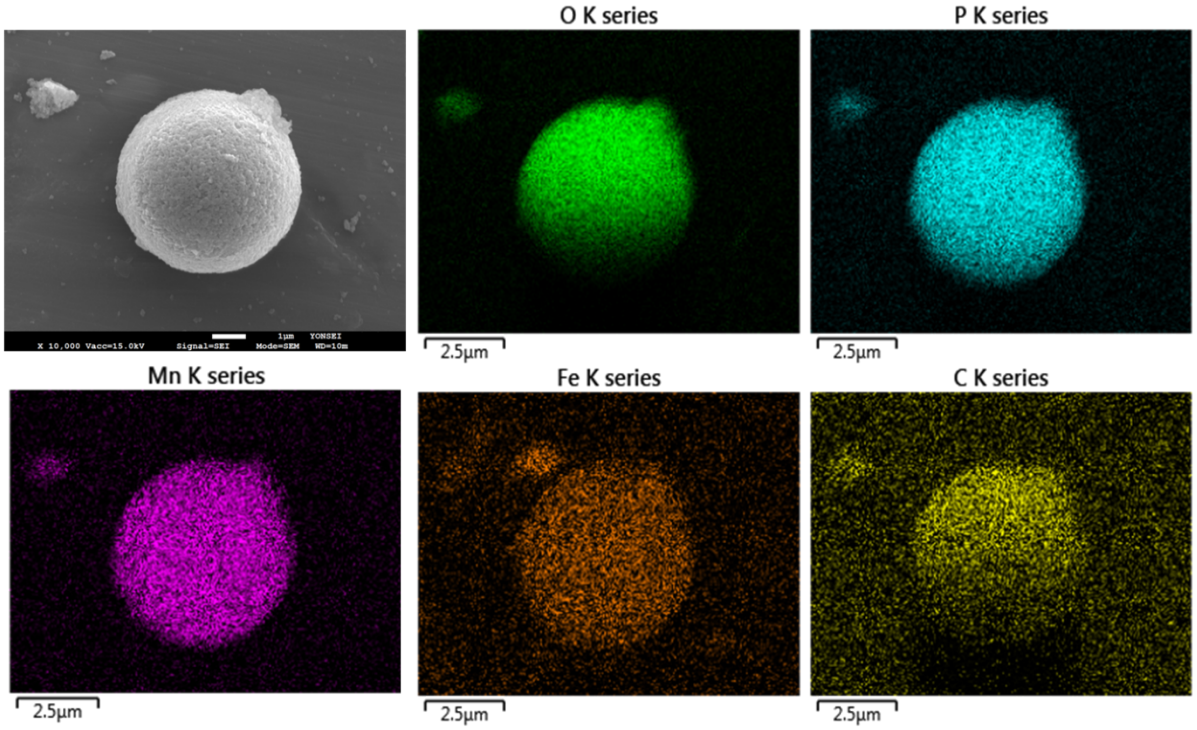

Fig. S1. EDS elemental mapping for $LiMn_{0.75}Fe_{0.25}PO_4/C$ microspheres prepared at a pH of 6.35.

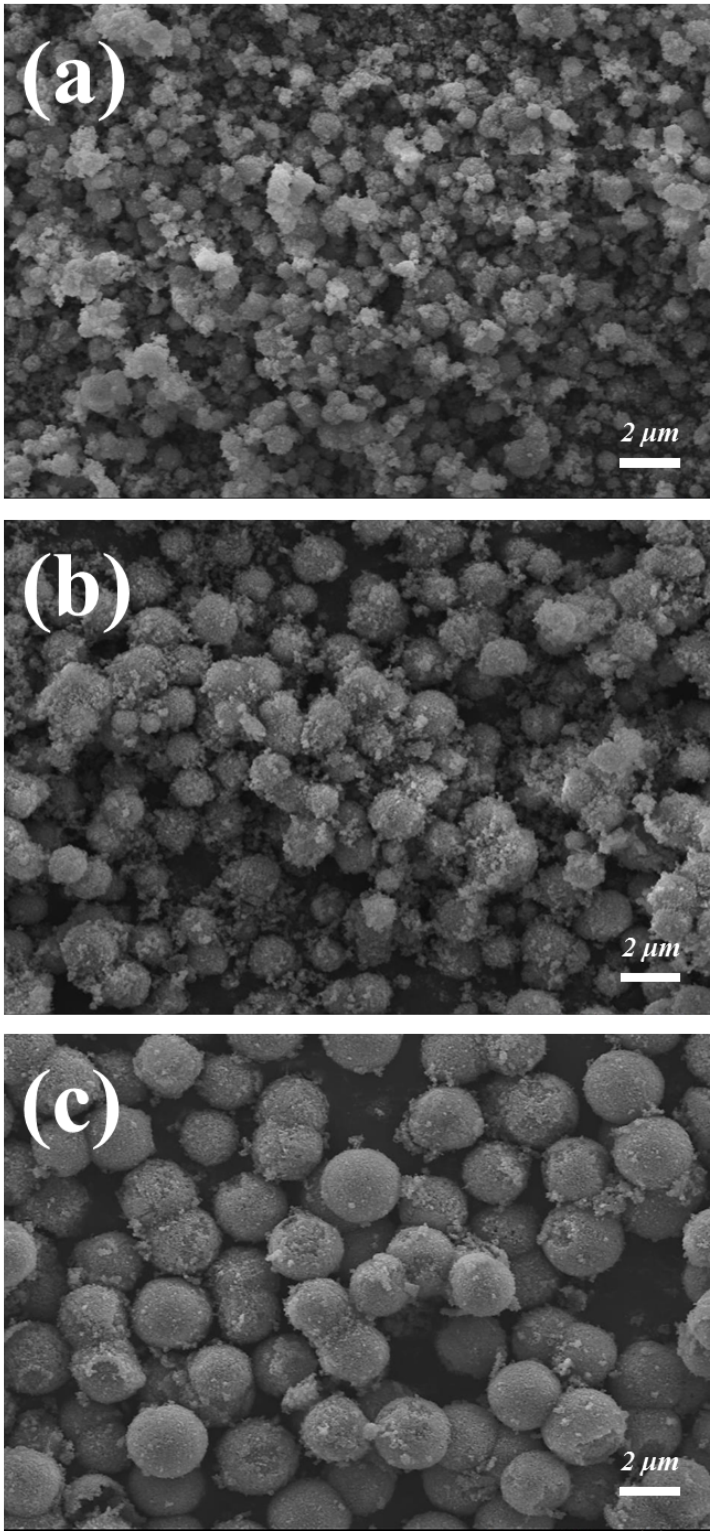

Fig. S2 (a-c) SEM images of the samples obtained at different reaction times: 1 min, 5 min, and 15 min, respectively.

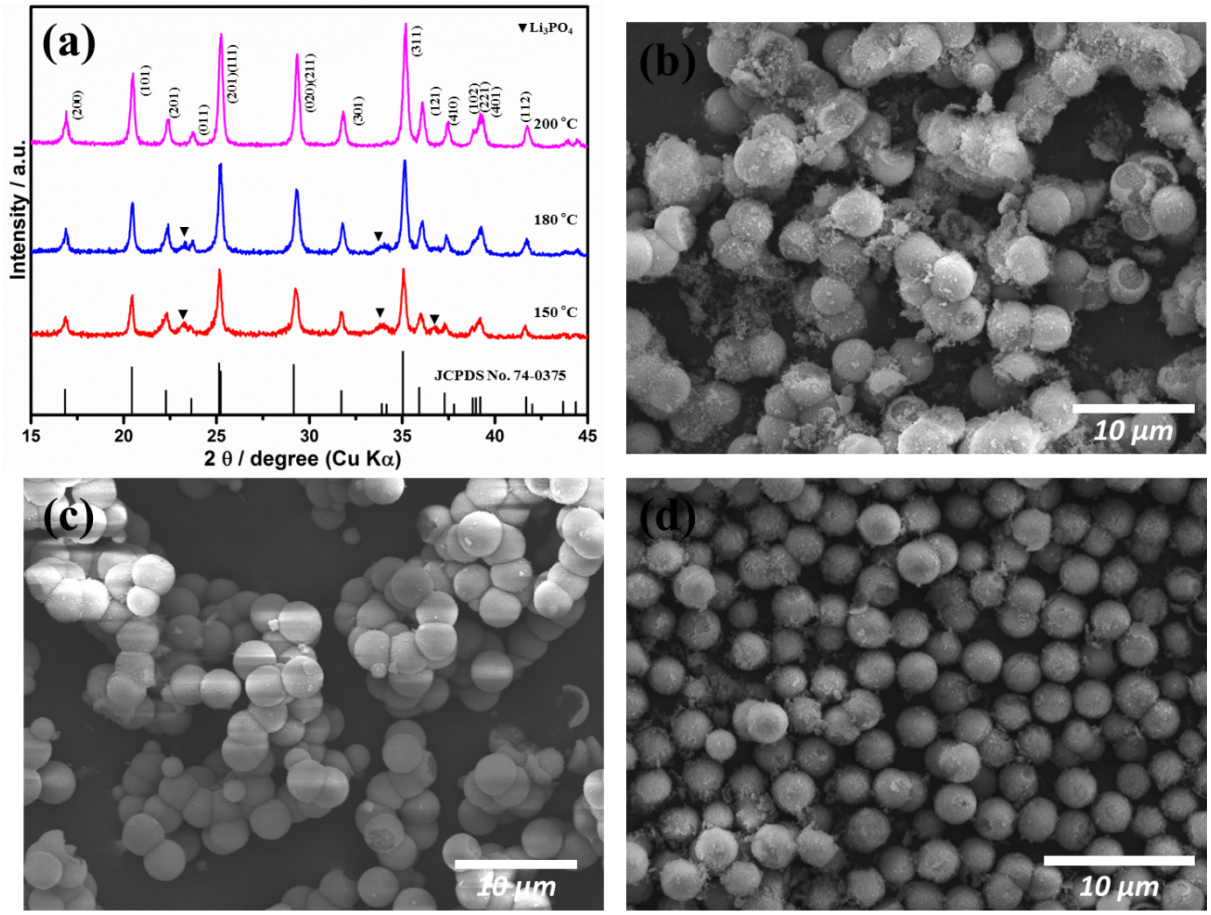

Fig. S3 (a) XRD patterns and (b-d) SEM images of the samples obtained at different reaction temperatures: 150 °C, 180°C, and 200°C, respectively.

To gain further insight into the effect of the temperature on the formation of microsized spherical particles, the pH of the precursor was fixed at 6.35 during the process. First, samples prepared at different temperatures were investigated by XRD. As shown in Fig. S3 (a), the diffraction peaks of the products prepared at 150 °C and 180 °C can be indexed as a mixture of $LiMn_{0.75}Fe_{0.25}PO_4$ and Li_3PO_4 (JCPDS card No. 25−1030). When the temperature is 200 °C, single-phase $LiMn_{0.75}Fe_{0.25}PO_4$ is obtained without the Li_3PO_4 phase. Fig. S3 (b) – (d) are SEM images. Although microspherical morphology of the sample prepared at 150 °C is dominant, with few unassembled small nanoparticles, the secondary particles agglomerated. When the temperature was increased to 180 °C, agglomerated microspheres were observed, as shown in Fig. S3 (c). When the temperature was increased to 200 °C, monodisperse $LiMn_{0.75}Fe_{0.25}PO_4$ microspheres were obtained. However, the microspherical morphology is dominant for all samples prepared at different temperatures.

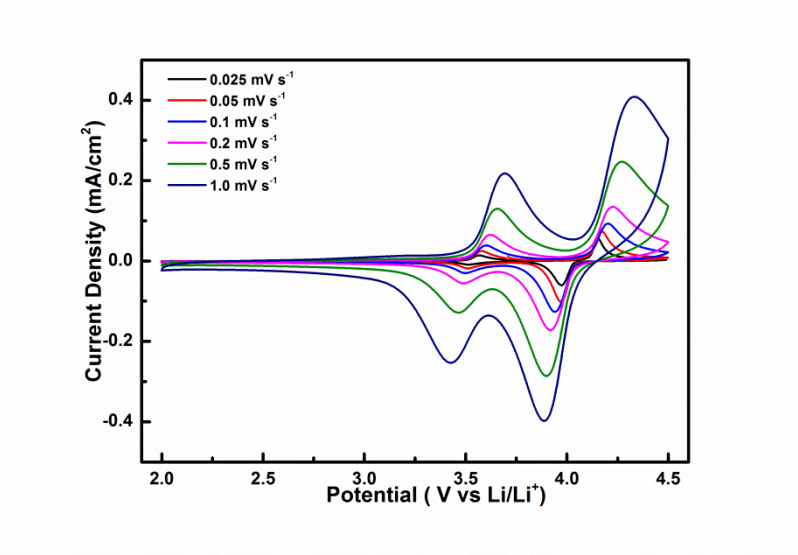

Fig. S4 Cyclic voltammograms (CVs) of $LiMn_{0.75}Fe_{0.25}PO_4/C$ microspheres (LMFP3) obtained at scan rates of 0.025, 0.05, 0.1, 0.2, 0.5, 1.0 mV s^{-1}.

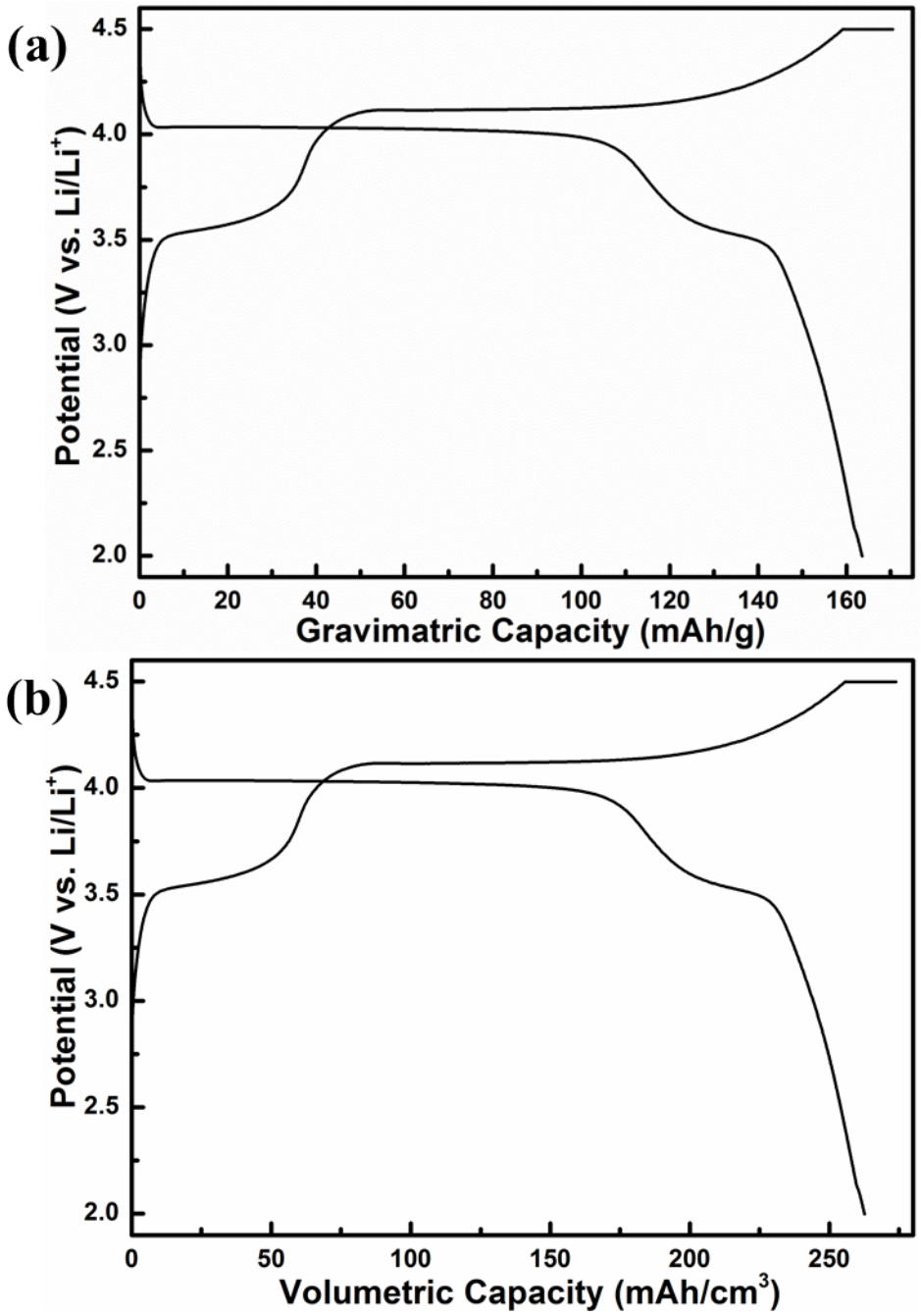

Fig. S5 Charge-discharge curves of $LiMn_{0.75}Fe_{0.25}PO_4$/C microspheres (LMFP3) obtained at 0.05 C-rate in terms of (a) gravimetric capacity and (b) volumetric capacity.

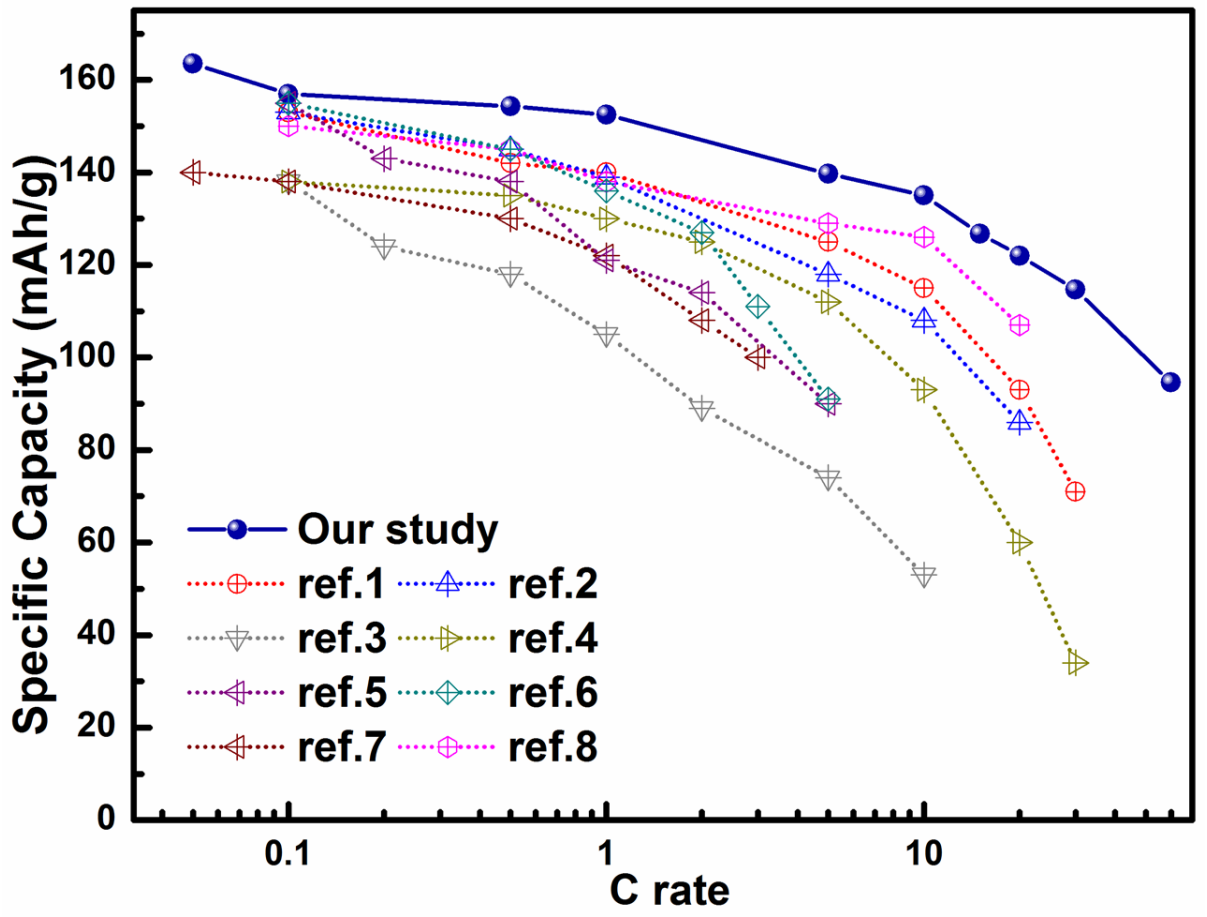

Fig. S6 Comparison of rate capabilities (discharge capacity versus discharge rate) of $LiMn_{0.75}Fe_{0.25}PO_4/C$ microspheres prepared in this study with those reported for microspherical $LiFePO_4/C$[1-5] and $LiMn_xFe_{1-x}PO_4/C$[6-8].

The $LiMn_{0.75}Fe_{0.25}PO_4/C$ microspheres prepared in this study showed a specific capacity of 100 mAh g^{-1} at an extremely high rate of 60 C-rate. This specific capacity is 57 % of the specific capacity at 0.05 C-rate, indicating the excellent high-rate capability of the prepared $LiMn_{0.75}Fe_{0.25}PO_4/C$ microspheres. We also compared the rate capabilities (discharge capacity versus discharge rate) of the $LiMn_{0.75}Fe_{0.25}PO_4/C$ microspheres prepared in this study with those reported for microspherical $LiFePO_4/C$ and $LiMn_xFe_{1-x}PO_4/C$. As shown in Fig. S6, the rate capabilities of $LiMn_{0.75}Fe_{0.25}PO_4/C$ microspheres prepared in this study were better than those found in previous studies.

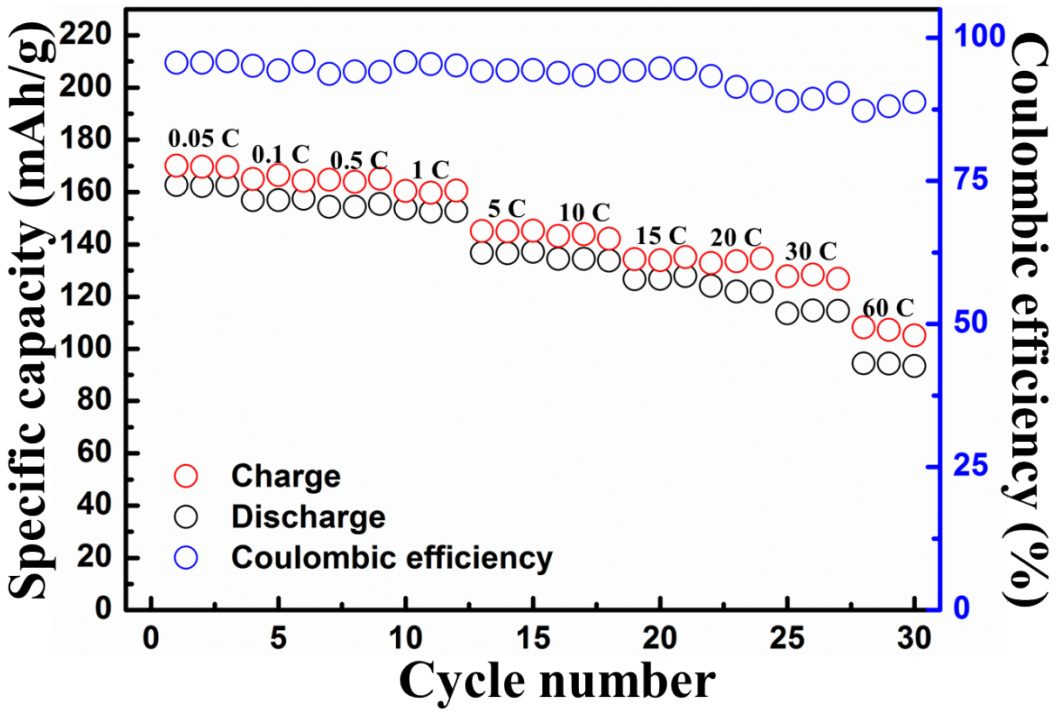

Fig. S7 Coulombic efficiency and specific capacity for different current rates (LMFP3).

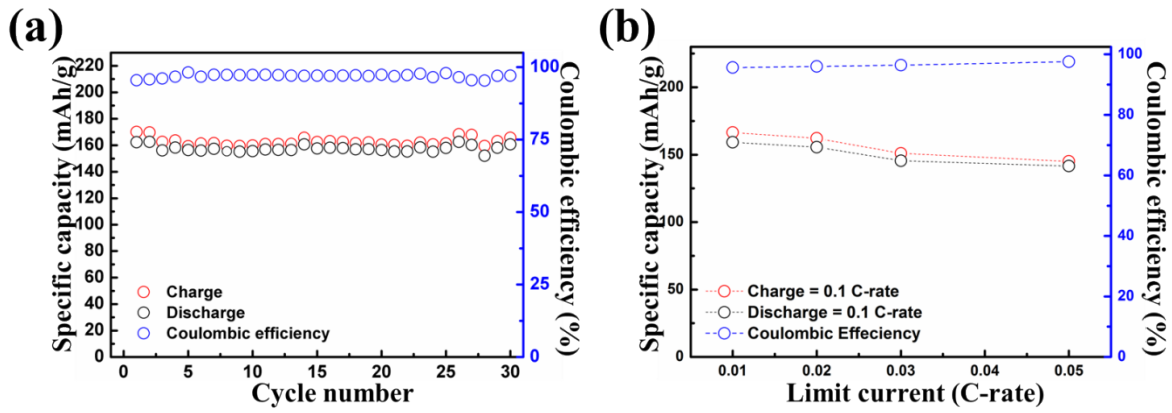

Fig. S8 (a) Cyclability at 0.05 C-rate over 30 cycles and (b) Coulombic efficiency and specific capacity of $LiMn_{0.75}Fe_{0.25}PO_4/C$ microspheres (LMFP3) at 0.1 C-rate for different limit currents.

Fig. S8 (a) shows the cycling stability of LMFP3 at a low rate of 0.05 C-rate over 30 cycles. The capacity retention after 30 cycles at 0.05 C-rate was 99.1%. And, the average coulombic efficiency was about 98 %. Fig. S8(b) shows the increase in coulombic efficiency and the decrease in specific capacity of $LiMn_{0.75}Fe_{0.25}PO_4/C$ microspheres (LMFP3) as the limit current is increased from 0.01 C-rate to 0.05 C-rate. At the limit current of 0.05 C-rate, the coulombic efficiency approaches 99 % with a slightly decreased specific capacity.

<References>

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