Supporting Information

Facile solvothermal synthesis of ultrathin $LiFe_xMn_{1-x}PO_4$ nanoplates as advanced cathodes with long cycle life and superior rate capability

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This file includes:

Synthesis of $LiFe_xMn_{1-x}PO_4$ (x=0.05, 0.10, 0.15)

Fig. S1–S6 and Table S1, S2

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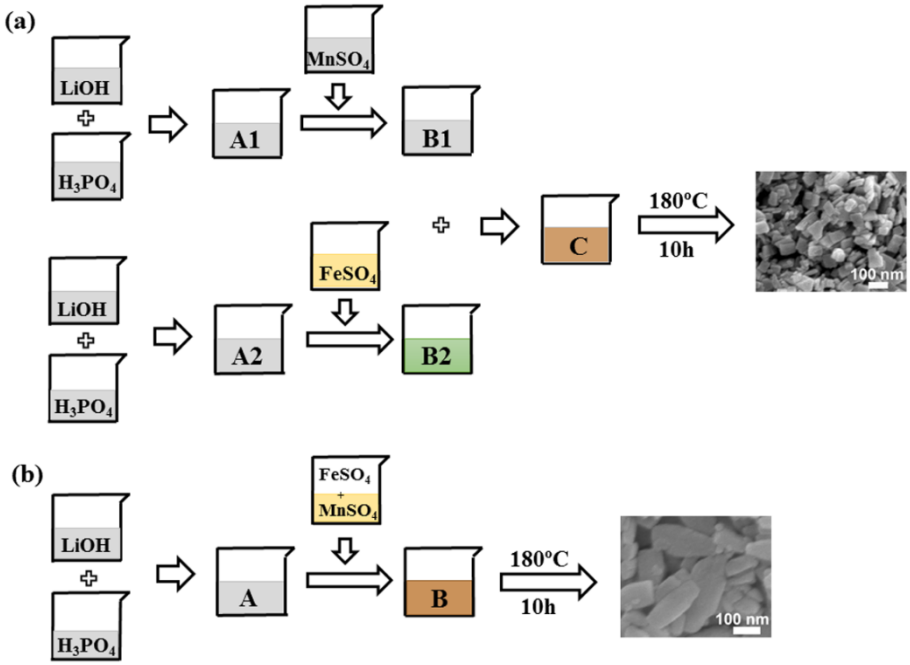
Preparation of $LiFe_xMn_{1-x}PO_4$ (x=0.05, 0.10, 0.15): For the synthesis of $LiFe_xMn_{1-x}PO_4$ (LFMP), a two-pot mixing route was first used to prepare the respective precursor solution of $LiMnPO_4$ and $LiFePO_4$, followed by mixing the two precursor solutions before the solvothermal reactions. In a typical synthesis of $LiFe_{0.1}Mn_{0.9}PO_4$ (LFMP-0.10), the preparation of the precursor solution of $LiMnPO_4$ can be divided into following steps: first, ethylene glycol (EG) solutions of LiOH and H_3PO_4 were prepared separately by dissolving LiOH (0.027 mol) in EG (10 mL) and H_3PO_4 (0.0099 mol) in EG (10 mL) with stirring (step 1); then, the H_3PO_4 solution was dropwise added to the LiOH solution with vigorous stirring to form solution A1 (step 2); afterwards, a $MnSO_4$ solution was prepared by dissolving $MnSO_4$ (0.009 mol) in a mixed solvent of deionized (DI) water (5 mL) and EG (5 mL) with stirring (step 3); finally, the $MnSO_4$ solution was added to solution A1 to form solution B1, the precursor solution of $LiMnPO_4$ (step 4). In a separate experiment, a mixed solution of LiOH and H_3PO_4 (solution A2) was first prepared by adding a EG (10 mL) solution of H_3PO_4 (0.0011 mol) to a EG (10 mL) solution of LiOH (0.003 mol) under stirring (step 5); then, a $FeSO_4$ solution, prepared by dissolving $FeSO_4$ (0.001 mol) in EG (10 mL), was added to solution A2 under vigorous stirring to form solution B2, the precursor solution of $LiFePO_4$ (step 6); finally, a mixed precursor solution (solution C) was prepared by mixing solution B1 and B2. After being stirred for 10 min, solution C was transferred to a Teflon-lined stainless steel autoclave (120 mL in capacity). The solvothermal reactions were conducted at 180 °C for 10 h. The white precipitate was collected by centrifugation, washed with DI water and absolute ethanol repeatedly, and dried at 60 °C for 12 h. $LiFe_{0.05}Mn_{0.95}PO_4$ (LFMP-0.05) and $LiFe_{0.15}Mn_{0.85}PO_4$ (LFMP-0.15) were synthesized with a similar method as $LiFe_{0.1}Mn_{0.9}PO_4$. For comparison, a one-pot mixing route was also applied to prepare the precursor solution of $LiFe_{0.1}Mn_{0.9}PO_4$ by combining steps 1,2 with step 5, and steps 3,4 with step 6. Namely, the solutions of $MnSO_4$ and $FeSO_4$ were mixed at the very beginning of the precursor preparation stage while the other steps are kept same. The resulting $LiFe_{0.1}Mn_{0.9}PO_4$ sample is named LFMP-0.10-A. Below is the schematic illustration of the synthetic route.



Schematic illustration of the synthetic route of $LiFe_xMn_{1-x}PO_4$: (a) two-pot precursors mixing route and (b) one-pot precursors mixing route.

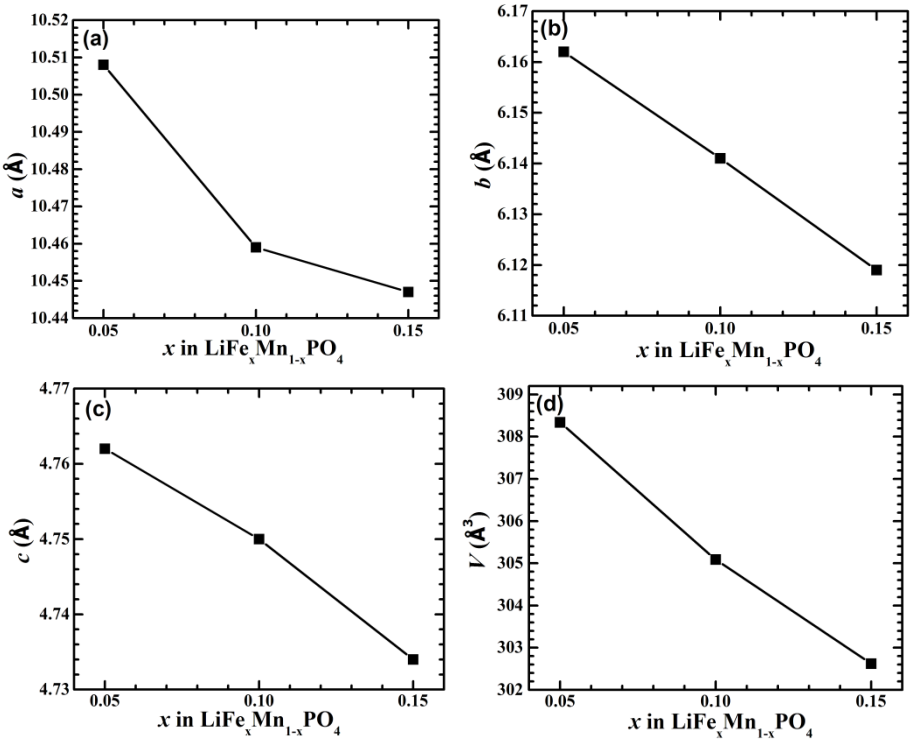


Fig. S1 Lattice parameters of $LiFe_xMn_{1-x}PO_4$ (x=0.05, 0.10, 0.15).

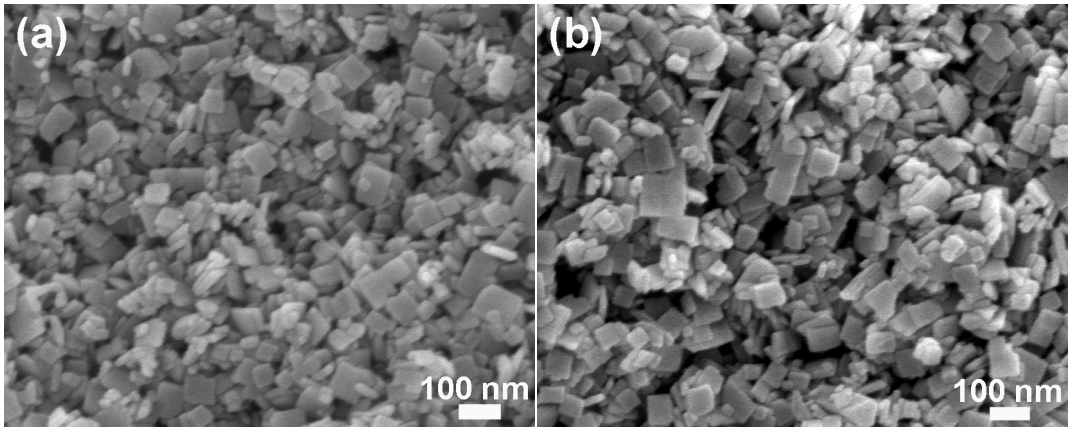


Fig. S2 SEM images of LFMP-0.05 and LFMP-0.10.

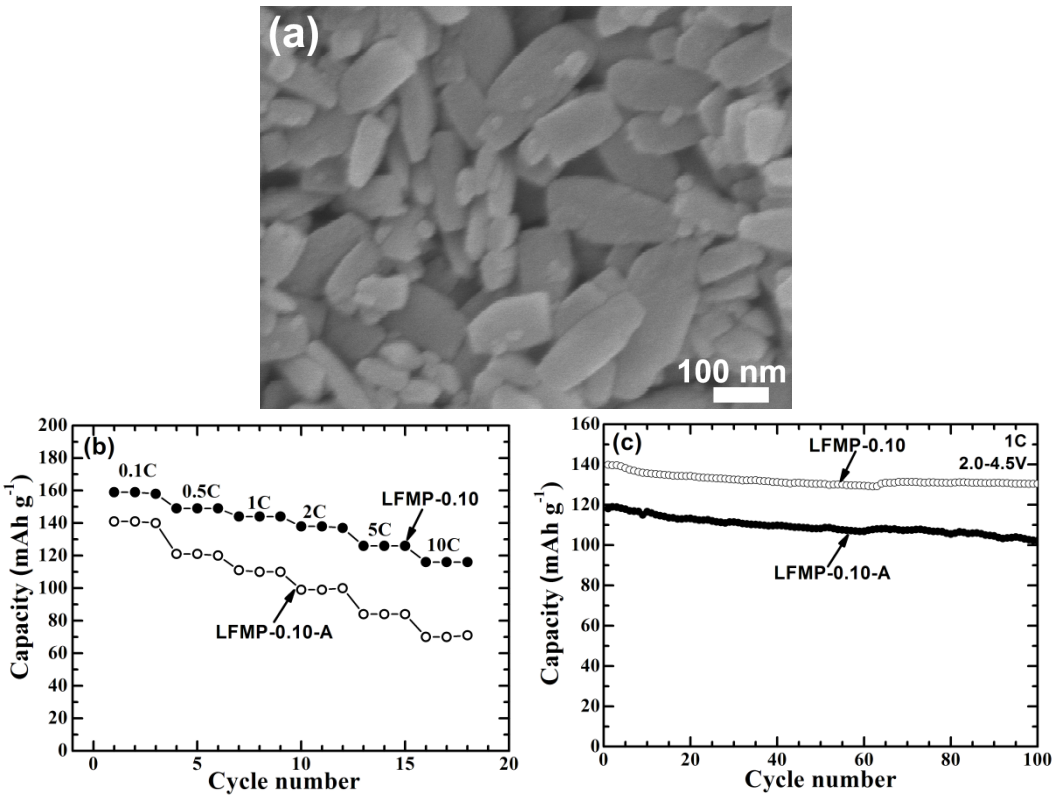


Fig. S3 (a) SEM image of LFMP-0.10-A and comparisons of (b) rate capability and (c) cycling stability between LFMP-0.10 and LFMP-0.10-A.

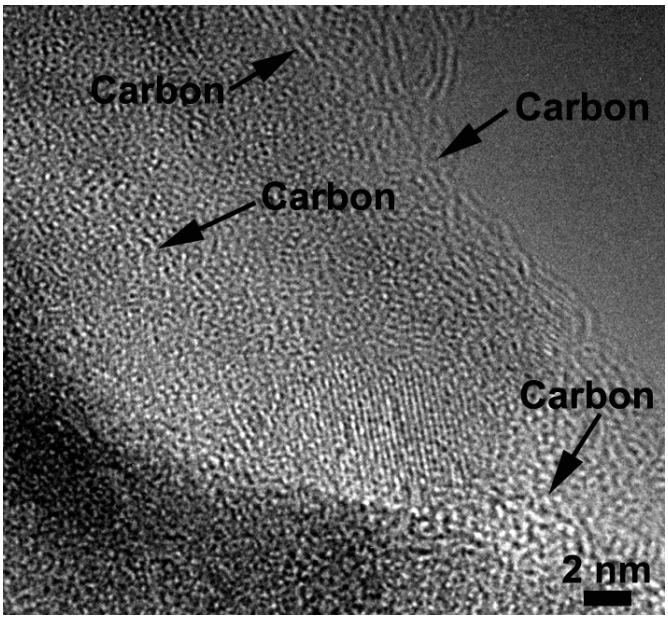


Fig. S4 HRTEM image of $LiFe_{0.15}Mn_{0.85}PO_4/C$ showing discrete carbon.

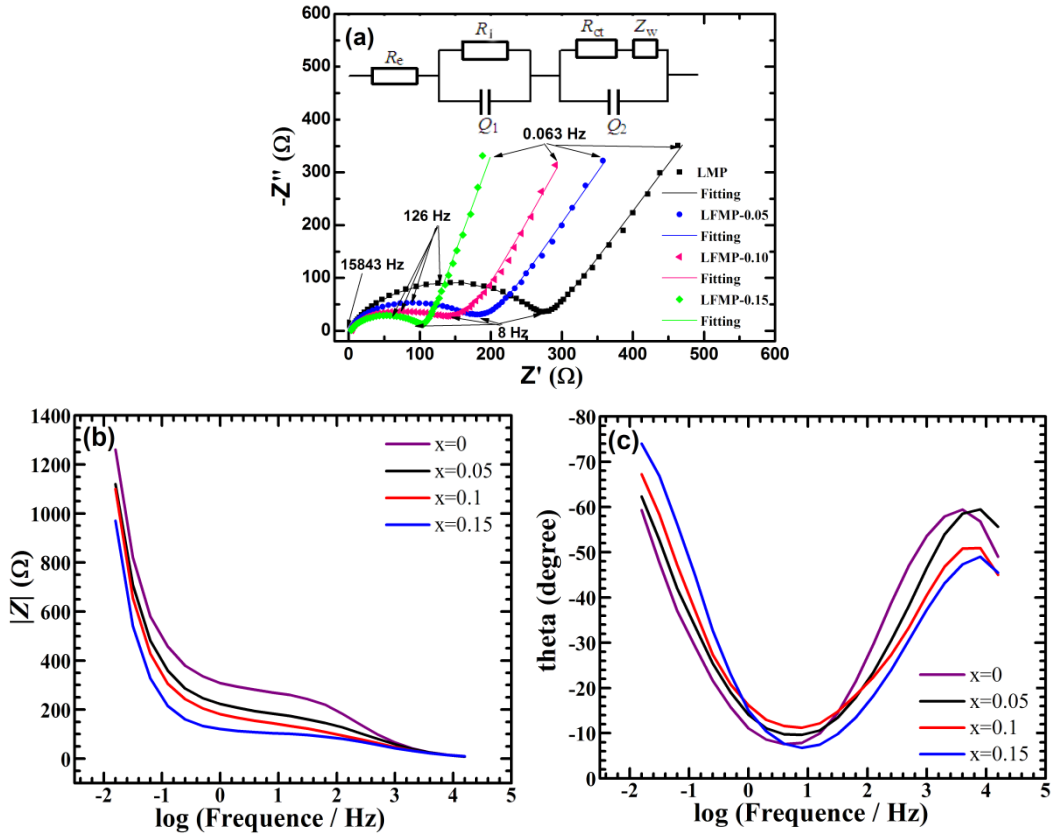


Fig. S5 (a) Nyquist plots and (b, c) Bode plots $LiFe_xMn_{1-x}PO_4/C$. The inset in (a) shows the equivalent circuit for the fitting of the Nyquist plot.

Table S1 Fitting results of the Nyquist plots using the equivalent circuit.

Sample	R_e (Ω)	R_i (Ω)	Q_1		R_{ct} (Ω)	Q_2	
			Y	n		Y	n
LMP	3.2	57.1	1.9×10^{-5}	0.85	223.4	3.0×10^{-5}	0.76
LFMP-0.05	1.5	75.1	1.4×10^{-5}	0.82	116.0	1.1×10^{-4}	0.70
LFMP-0.10	2.5	55.7	2.1×10^{-5}	0.80	108.5	3.0×10^{-4}	0.61
LFMP-0.15	1.8	46.7	3.5×10^{-5}	0.73	63.5	2.0×10^{-4}	0.62

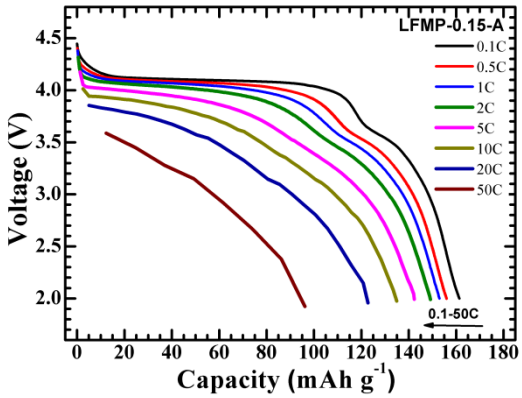


Fig. S6 Rate capability of the LFMP-0.15-A sample tested at lower carbon content. In this sample the coated carbon on LFMP-0.15-A is reduced to 6 wt% from 9wt% by reducing the amount of sucrose. For electrochemical test, the LFMP-0.15-A/PVDF/AB weight ratio is 75:10:15 instead of 70:10:20.

Table S2 Comparisons of cycling stability of $LiFe_xMn_{1-x}PO_4/C$ ($x \leq 0.15$).

Sample	Charge and discharge rate	Carbon content (wt%)	Cycle number	Capacity retention	Reference
x=0	Charge-0.05C Discharge-0.5C	27.43	50	88%	[1]
x=0	0.5C	7.0	100	87.9%	[2]
x=0	1C	–	200	95%	[3]
x=0.05	**10C**	**9**	**1000**	**64.3%**	**This work**
x=0.05	0.1C	10	50	93.9%	[4]
x=0.1	**10C**	**9**	**1000**	**65.3%**	**This work**
x=0.1	Charge-0.1C Discharge-10C	10–12	100	75%	[5]
x=0.1	0.5C	3.69	70	74.4%	[6]
x=0.15	**10C**	**9**	**1000**	**69.4%**	**This work**
x=0.15	1C	–	500	89%	[7]
x=0.15	Charge-0.05C Discharge-0.5C	–	50	~92.7%	[8]

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