

Supplementary Information

Improving $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ Nanoplates Performances by a Dual Modification Strategy Toward Practical Application of Li-ion Batteries

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1、 Physicochemical characterization

The morphology and microstructure were characterized by the scanning electron microscope (SEM, ZEISS Merlin, at 10 kV) and transmission electron microscope (TEM, Thermo Scientific Talos F200X G2, at 200 kV). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM, Thermo Scientific Talos F200X G2) was used to further study the elemental distribution of the materials. The X-ray diffraction (XRD) patterns were obtained using a Rigaku MiniFlex 600 X-ray diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$). The X-ray photoelectron spectroscopy (XPS) was carried out with a multi-technique system using an Al monochromatic X-ray at a power of 350 W (Thermo Scientific K-Alpha). The binding energy of the spectra was calibrated by using the C 1s (284.6 eV).

2、 Electrochemical measurements

2032-type coin cells were used to evaluate the electrochemical performances of synthesized samples. The cathode slurry was prepared by dispersing 80 wt% of active material, 10 wt% of poly-vinylidene fluoride (PVDF) and 10 wt% of super P in N-methyl-2-pyrrolidone (NMP). Then, slurry was uniformly casted onto pure Al foil and dried at 120 °C in vacuum oven for 12 hours. The half-cell was assembled in an Ar-filled glove box using prepared cathode, Celgard 2500 membrane and lithium foil as working electrode, separator and counter electrode, respectively. The electrolyte was 1.0 M LiPF₆ solution with ethylene carbonate (EC) + dimethyl carbonate (DMC) + ethylmethyl carbonate (EMC) (v/v/v = 1:1:1). Charge-discharge measurement was performed on battery test equipment (NEWARE, CT/CTE-4000) at a specific C rate (1 C=170 mAh g⁻¹) using a constant-current constant-voltage (CC-CV) protocol in a voltage of 2.4~4.5 V (vs. Li⁺/Li). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed on Gamry-3000 electrochemical workstation. The frequency of EIS test is from 100 kHz to 10 mHz using an AC voltage of 5 mV amplitude. All the experiments for electrochemical performances were performed on constant temperature at 25 °C.

Supplementary figures

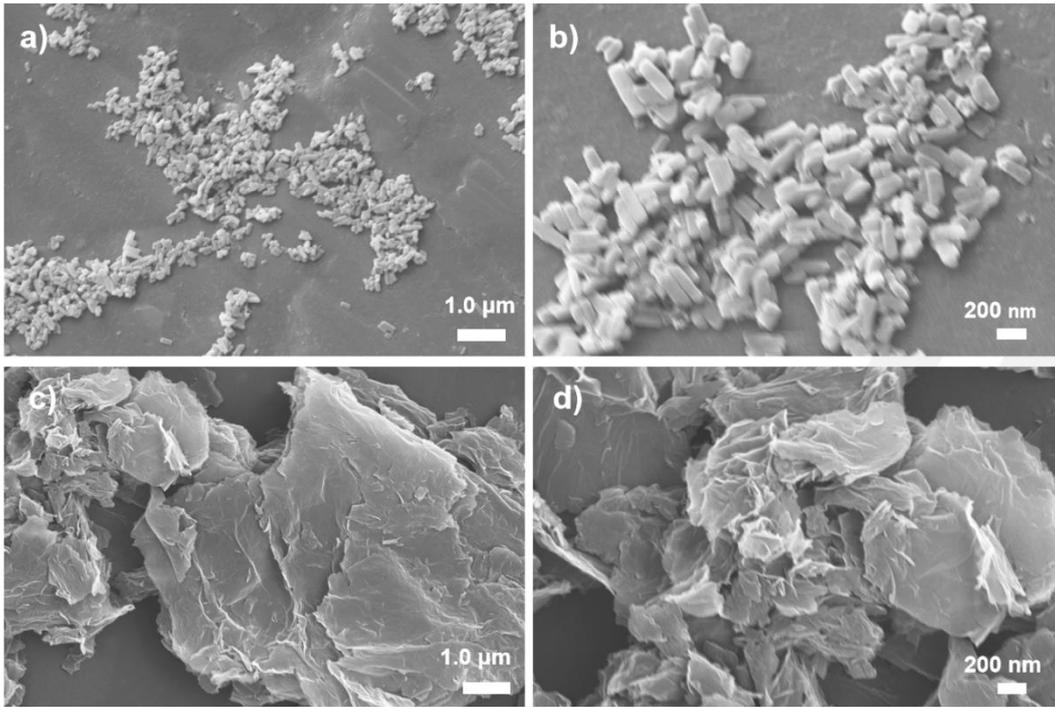


Figure S1. a-b) SEM image of the LMFP/C-F/G nanorods and c-d) graphene.

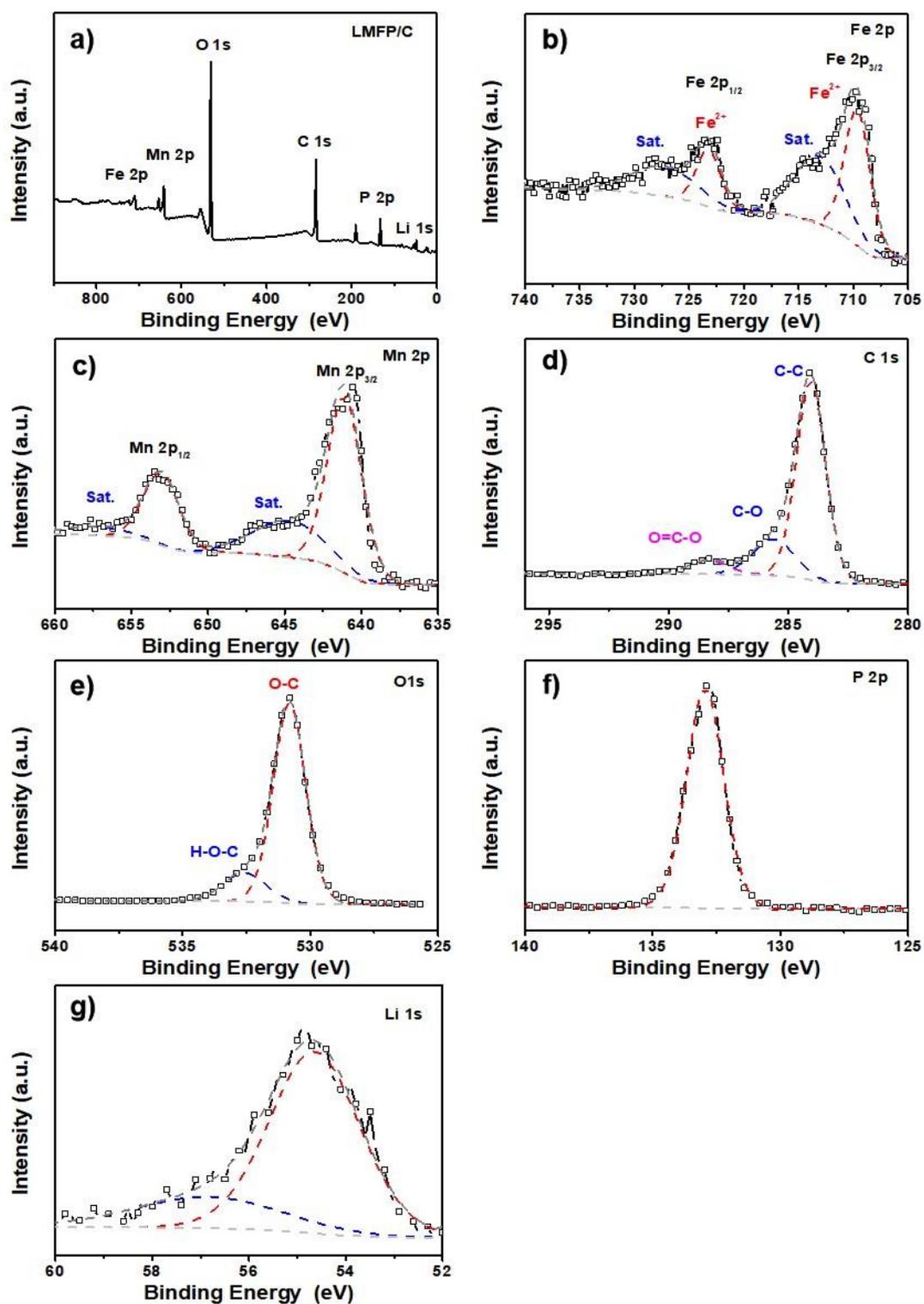


Figure S2. a) XPS survey spectra of LMFP/C and the high-resolution spectrum of b) Fe 2p; c) Mn 2p; d) C 1s; e) O 1s; f) P 2p; g) Li 1s.

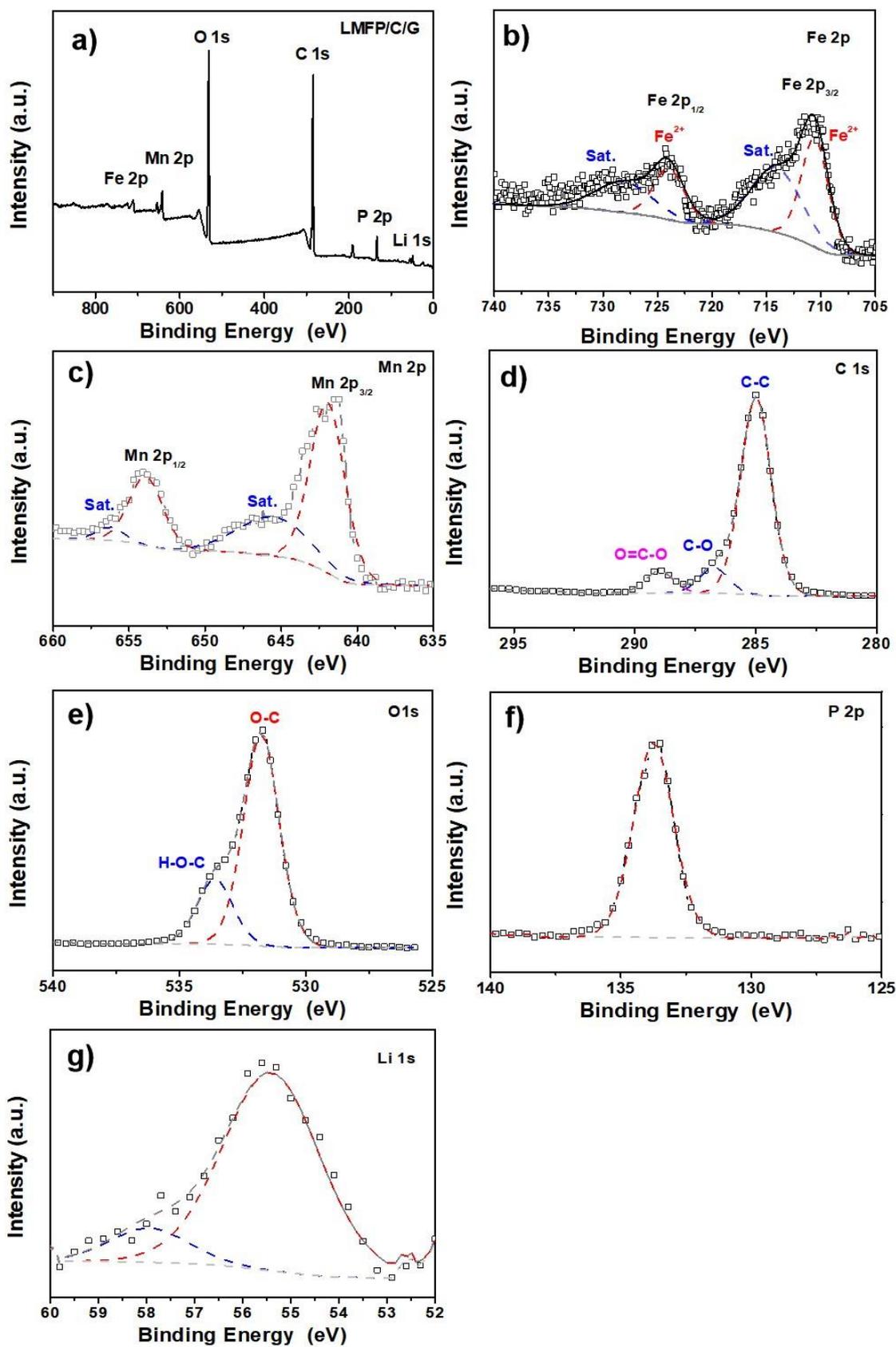


Figure S3. a) XPS survey spectra of LMFP/C/G and the high-resolution spectrum of b) Fe 2p; c) Mn 2p; d) C 1s; e) O 1s; f) P 2p; g) Li 1s.

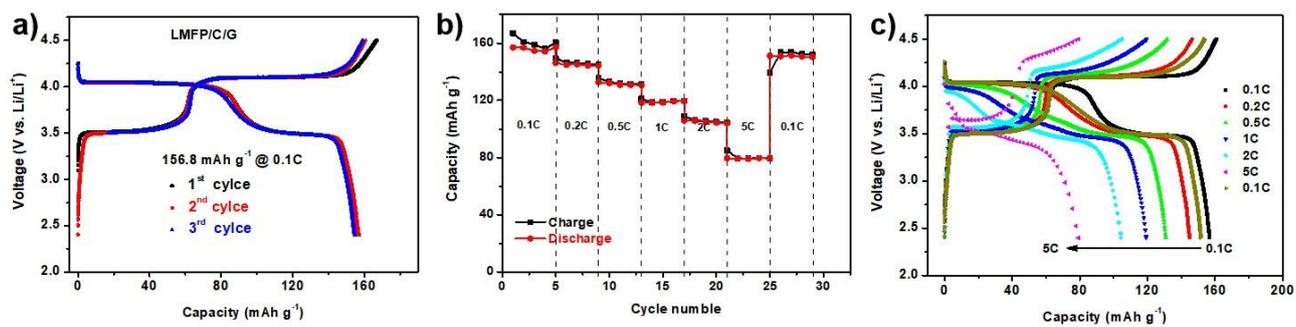


Figure S4. Electrochemical performance of LMFP/C/G at 25 °C: a) First three charge/discharge profiles at 0.1 C; b) Rate performance at different C rates and c) Corresponding charge/discharge curves.

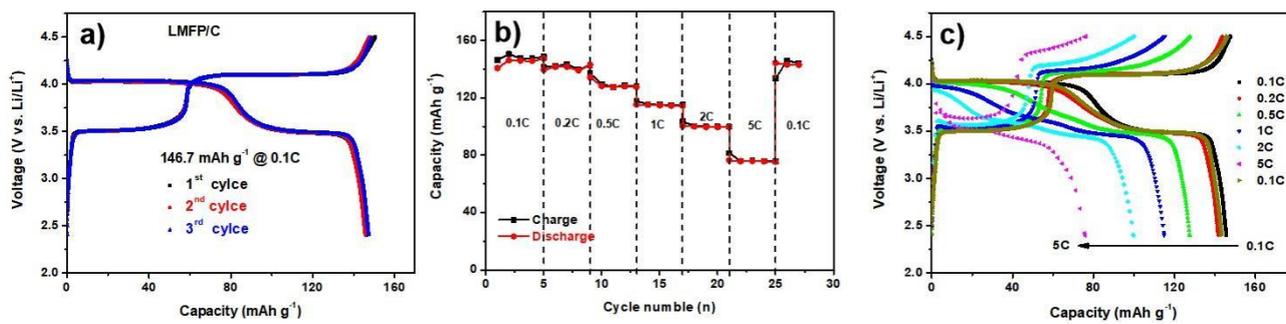


Figure S5. Electrochemical performance of LMFP/C at 25 °C: a) First three charge/discharge profiles at 0.1 C; b) Rate performance at different C rates and c) Corresponding charge/discharge curves.

Supplementary tables

Table S1. The discharge capacity at different C rates and corresponding energy density of the three materials were studied.

Sample	0.1C	0.2C	0.5C	1C	2C	5C	Energy density (Wh kg ⁻¹)
LMFP/C	146.7	142.8	132.6	118.2	101.2	78.9	564.8
LMFP/C/G	157.8	146.3	135.4	119.6	107.5	81.2	615.4
LMFP/C-F/G	163.1	155.7	146.7	130.1	114.6	88.1	639.4

Table S2. The lithium ion diffusion coefficient D_{Li+} of the cathode materials were calculated from the Randles-Sevcik formula.

Materials	Parameter	Mn Oxidation site	Mn Reduction site	Fe Oxidation site	Fe Reduction site
LMFP/C-F/G		1.71	-1.24	3.04	-2.17
LMFP/C/G	slope	1.24	-0.91	1.87	-1.51
LMFP/C		0.6	-0.32	1.13	-1.17
LMFP/C-F/G		2.73×10^{-7}	1.98×10^{-7}	4.85×10^{-7}	3.46×10^{-7}
LMFP/C/G	$D^{1/2}$	1.98×10^{-7}	1.45×10^{-7}	2.98×10^{-7}	2.41×10^{-7}
LMFP/C		9.57×10^{-8}	5.11×10^{-8}	1.80×10^{-7}	1.87×10^{-7}
LMFP/C-F/G		7.45×10^{-14}	3.92×10^{-14}	2.35×10^{-13}	1.20×10^{-13}
LMFP/C/G	D ($\text{cm}^2 \text{s}^{-1}$)	3.92×10^{-14}	2.11×10^{-14}	8.90×10^{-14}	5.81×10^{-14}
LMFP/C		9.17×10^{-15}	2.61×10^{-15}	3.25×10^{-14}	3.48×10^{-14}

Table S3. Comparison of properties of LMFP materials.

Materials	Methods	Particle size	Initial discharge capacity (mAh g ⁻¹)	Median discharge voltage (V)	Energy density (Wh kg ⁻¹)	Ref.
LMFP/C	Solvothermal		146.7@0.1C	3.85	564.8	This work
LMFP/C/G	synthesis+calcination	50-400 nm	157.8@0.1C	3.90	615.4	This work
LMFP/C-F/G	ns (600 °C for 4 h in Ar)		163.1@0.1C	3.92	639.4	This work
LiFe _{0.5} Mn _{0.5} P O ₄ / (C+rGO)	Solvothermal synthesis+calcination ns	~100 nm	166.0@0.1C	3.65	605.9	Journal of Power Sources [1]
LiFe _{0.5} Mn _{0.5} P O ₄ /C	Solvothermal synthesis+calcination ns	~200 nm	155.0@0.1C	3.65	565.7	Journal of Materials Chemistry A [2]
LiFe _{0.2} Mn _{0.8} P O ₄ / (C+NG)	Co-precipitation method	50-100 nm	159.1@0.1C	3.92	624.5	Electrochimica Acta [3]
LiFe _{0.3} Mn _{0.7} P O ₄ /rGO@C	Co-precipitation method+calcinations (700 °C for 1 h in H ₂ /Ar=3/97)	200 nm	161@0.1C	3.95	635.9	ACS Applied Energy Materials [4].
Li _{1-x} Na _x Mn _{0.8} Fe _{0.2} PO ₄ /C	Solvothermal synthesis	40-120 nm	141.4@0.1C	4.05	572.7	Ceramics International [5]
LiFe _{0.15} Mn _{0.85} PO ₄ /C	Solvothermal synthesis	40-100 nm	165.4@0.1C	4.0	661.6	Journal of Materials Chemistry A [6].

Table S3. Comparison of properties of LMFP materials.

Materials	Methods	Particle size	Initial discharge capacity (mAh g ⁻¹)	Median discharge voltage (V)	Energy density (Wh kg ⁻¹)	Ref.
Mg-doped LiMn _{0.8} Fe _{0.2} PO ₄ /C	Solvothermal method +calcinations (600 °C for 4 h in H ₂ /Ar=5/95)	~200 nm	156.9@0.1C	3.95	619.75	Journal of Energy Storage [7]
LiFe _{0.2} Mn _{0.8} PO ₄ /C	Polyol method+ calcinations (680 °C for 1 h in H ₂ /Ar=2/98)	20-80 nm	160.6@0.1C	3.9	626.3	RSC Advances [8]
LiFe _{0.5} Mn _{0.5} PO ₄ /C	Solvothermal synthesis +calcinations (600 °C for 5 h in N ₂)	100-300 nm	157.6@0.1C	3.7	583.1	Electrochemistry Communications [9]
LiFe _{0.5} Mn _{0.5} PO ₄ /C	Solvothermal synthesis +calcinations (600 °C for 5 h in N ₂)	100-300 nm	157.0@0.1C	3.8	596.6	Electrochemistry Communications [9]

References

1. Xiang, W.; Wu, Z. G.; Wang, E. H.; Chen, M. Z.; Song, Y.; Zhang, J. B.; Zhong, Y. J.; Chou, S. L.; Luo, J. H.; Guo, X. D., Confined Synthesis of Graphene Wrapped $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ Composite Via Two Step Solution Phase Method as High Performance Cathode for Li-ion Batteries. *Journal of Power Sources* **2016**, 329, 94-103.
2. Chi, Z. X.; Zhang, W.; Wang, X. S.; Cheng, F. Q.; Chen, J. T.; Cao, A. M.; Wan, L. J., Accurate Surface Control of Core–Shell Structured $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4@\text{C}$ for Improved Battery Performance. *Journal of Materials Chemistry A* **2014**, 2, 17359-17365.
3. Wen, F.; Lv, T. a.; Gao, P.; Wu, B.; Liang, Q.; Zhang, Y.; Shu, H.; Yang, X.; Liu, L.; Wang, X., Graphene-Embedded $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4$ Composites with Promoted Electrochemical Performance for Lithium Ion Batteries. *Electrochimica Acta* **2018**, 276, 134-141.
4. Ding, D.; Maeyoshi, Y.; Kubota, M.; Wakasugi, J.; Kanamura, K.; Abe, H., A Facile Way To Synthesize Carbon-Coated $\text{LiMn}_{0.7}\text{Fe}_{0.3}\text{PO}_4$ /Reduced Graphene Oxide Sandwich-Structured Composite for Lithium-Ion Batteries. *ACS Applied Energy Materials* **2019**, 2, 1727-1733.
5. Li, R.; Fan, C.; Zhang, W.; Tan, M.; Zeng, T.; Han, S., Structure and Performance of Na^+ and Fe^{2+} Co-Doped $\text{Li}_{1-x}\text{Na}_x\text{Mn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ Nanocapsule Synthesized by a Simple Solvothermal Method for Lithium ion Batteries. *Ceramics International* **2019**, 45, 10501-10510.
6. Liao, L.; Wang, H.; Guo, H.; Zhu, P.; Xie, J.; Jin, C.; Zhang, S.; Cao, G.; Zhu, T.; Zhao, X., Facile Solvothermal Synthesis of Ultrathin $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ Nanoplates as Advanced Cathodes with Long Cycle Life and Superior Rate Capability. *Journal of Materials Chemistry A* **2015**, 3, 19368-19375.
7. Hu, H.; Li, H.; Lei, Y.; Liu, J.; Liu, X.; Wang, R.; Peng, J.; Wang, X., Mg-doped $\text{LiMn}_{0.8}\text{Fe}_{0.2}\text{PO}_4/\text{C}$ Nano-Plate as a High-Performance Cathode Material for Lithium-ion Batteries. *Journal of Energy Storage* **2023**, 73, 109006.
8. Xu, H.; Zong, J.; Ding, F.; Lu, Z. W.; Li, W.; Liu, X. J., Effects of Fe^{2+} ion Doping on LiMnPO_4 Nanomaterial for Lithium ion Batteries. *RSC Advances* **2016**, 6, 27164-27169.
9. Wang, K.; Hou, M.; Yuan, S.; Yu, H.; Wang, Y.; Wang, C.; Xia, Y., An Additional Discharge Plateau of Mn^{3+} in $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ at High Current Rates. *Electrochemistry Communications* **2015**, 55, 6-9.