Supporting Information

Achieving long-lasting and high-capacity $LiFe_{0.5}Mn_{0.5}PO_4$ cathodes with a synergistic F/In dual doping strategy

Zepeng Li[a,b], Jianhui Zhu[c], Maowen Xu[a]* and Jian Jiang[a,b,d]*

[a]*School of Materials and Energy, and Chongqing Key Lab for Advanced Materials and Clean Energies of Technologies, Southwest University, No. 2 Tiansheng Road, BeiBei District, Chongqing 400715, P.R. China.*

[b]*Guizhou Phosphate New Energy Technology Co., Ltd., Fuquan 550501, China.*

[c]*School of Physical Science and Technology, and Chongqing Key Laboratory of Micro & Nano Structure Optoelectronics, Southwest University, No. 2 Tiansheng Road, BeiBei District, Chongqing 400715, P.R. China.*

[d]*College of Chemistry and Chemical Engineering, Key Laboratory of Laser Technology and Optoelectronic Functional Materials of Hainan Province, and Key Laboratory of Functional Materials and Photoelectrochemistry of Haikou, Hainan Normal University, Haikou 571158, China.*

To whom correspondence should be addressed: Tel: +86-23-68254842.

**E-mail: xumaowen@swu.edu.cn (M. Xu); jjiang@swu.edu.cn (J. Jiang).*

1. Experimental Section

1.1 Materials Synthesis

The F/In co-doped $LiFe_{0.5}Mn_{0.5}PO_4$ (denoted as F/In-LFMP) powder samples are prepared by a conventional solid-state reaction. For details, 0.74 g Li_2CO_3 (*Adamas*), 1.75 g $MnC_2O_4{\cdot}2H_2O$ (*Adamas*), 1.80 g $FeC_2O_4{\cdot}2H_2O$ (*Macklin*), 2.30 g $NH_4H_2PO_4$ (*Macklin*), 0.028 g In_2O_3 (*Adamas*), 0.022 g NH_4F (*Macklin*) and 1.0 g glucose (*Macklin*) are mixed with 15 mL ethanol. This mixture is then mechanically ground by a planetary mill (rate: 600 r min^{-1}; operation time: 6 h). The milled products are dried and heated at 350 ℃ for 3 h, followed

by an annealing treatment at 650 ℃ for 10 h under Ar atmospheres to form F/In-LFMP. The other parallel samples of $LiFe_{0.5}Mn_{0.5}PO_4$ (LFMP), $LiFe_{0.5}Mn_{0.5}PO_{3.97}F_{0.03}$ (F-LFMP), and $LiFe_{0.5}Mn_{0.49}In_{0.01}PO_4$ (In-LFMP) are made by the same solid-state reactions, except for the selective addition of In_2O_3 or NH_4F.

1.2 Samples Characterization

The crystallographic phases of samples are characterized by X-ray diffraction (XRD, *Shimadzu*-7000 with Cu Kα radiation, λ=1.5406 Å) at a scan rate of 5° min^{-1} in the 2θ range of 10-80°. The in-situ XRD testing is conducted in an electrochemical window of 2.5–4.5 V (Bruker D8 Advance), using a Be foil to seal the cell device. Each XRD spectrum is collected within 13 min. The structural parameters are analyzed by Rietveld refinement using the GSAS-II software. The thermogravimetric analysis (TGA-Q50, TA Instruments; heating rate: 10 ℃ min^{-1}; sensitivity: 0.1 μg, USA) is carried out with a platinum pan under a N_2 flow (rate: 40 mL min^{-1}). The samples morphology and microstructures are examined by the transmission electron microscopy (TEM, FEI Tecnai F20) and field-emission scanning electron microscopy (FESEM, JEOL JSM-7800F) equipped with an energy-dispersive X-ray spectroscopy (EDS). The XPS (Thermo Scientific K-Alpha) technique is used to determine the chemical state of elements. The electronic conductivity of cathode powders is measured by a 4-probe DC device (model: ST2742B).

1.3 Electrochemical Measurements

The electrochemical testing is performed using the CR2032-type coin cells at room temperature. The active materials, acetylene black, and polyvinylidene fluoride (PVDF) are mixed at a weight ratio of 8:1:1 and dispersed in N-methyl pyrrolidone (NMP) solvent to obtain the homogeneous slurry. Then, the slurry is coated onto the aluminum foil (actives loading density: ~2.5 mg cm^{-2}) and dried in a vacuum oven for 10 h at 60 °C. Cells are assembled in an Ar-filled glove box, using the electrolyte of 1 mol L^{-1} $LiPF_6$ dissolved Ethylene Carbonate/Ethyl Methyl Carbonate/Dimethyl Carbonate (EC/EMC/DMC, 1:1:1 by volume) with 1% Vinylene

Carbonate (VC). The Li foil (thickness: 100 μm) is used as the reference/counter electrode, and a polypropylene microporous film (Celgard 2400, USA) serves as the separator. The total amount of electrolyte injected into each coin-type cell is ~35 μL. The cyclic voltammetry (CV) measurements (voltage window: 3.0-4.7 V *vs.* Li/Li^+) and the electrochemical impedance spectroscopy (frequency range: 100 kHz-0.1 Hz) are performed on a CS310 electrochemical workstation. All the galvanostatic measurements are conducted on Land CT2001A battery testers in a voltage range of 2.5-4.5 V at 25 °C.

1.4 Computational Methods

The involved DFT calculations are performed by the Vienna Ab initio simulation package (VASP) 5.4.4 program with the GGA-PBE exchange-correlation functionals. The core-electron interaction is described by the projector augmented wave (PAW) method, and the spin polarization is considered. The PBEsol function is augmented with a *Hubbard* on-site potential (U = 4.3 for Fe and 4.5 eV for Mn) by a general LDA+U approach. The cut-off energy is set to be 520 eV, and the k points for the Brillouin zone are set as 5 × 3 × 3. The Gaussian smearing width is set to 0.2 eV. The cell parameters and geometries of all structures are optimized until the energy is converged to 1×10^{-4} eV.

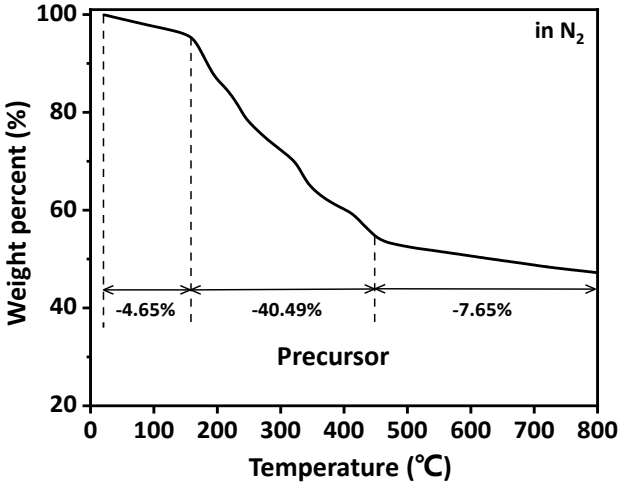

Fig. S1 TGA plot of precursors during the calcination process.

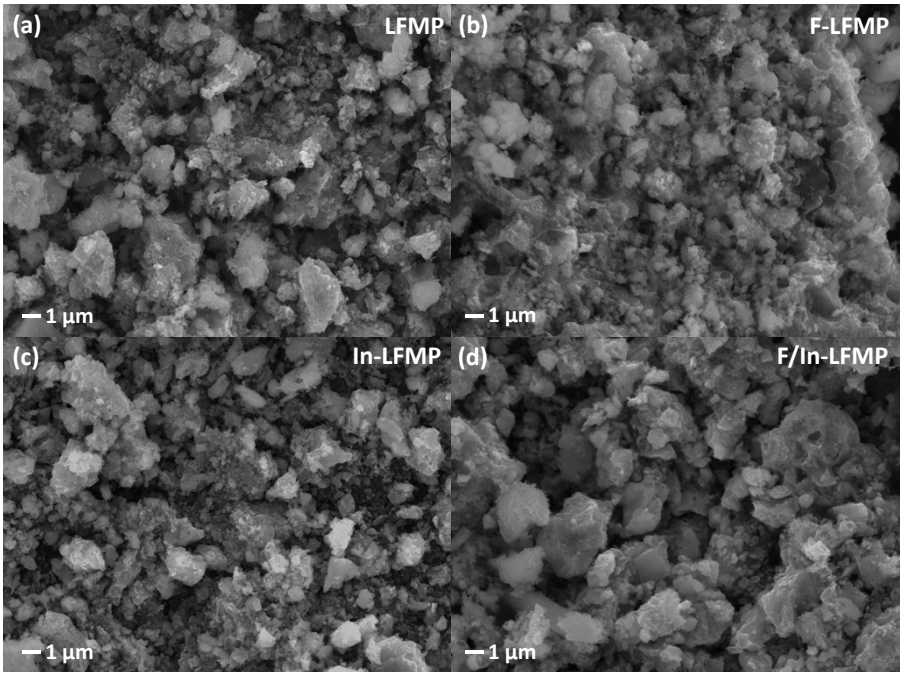

Fig. S2 Typical SEM images of (a) LFMP, (b) F-LFMP, (c) In-LFMP and (d) F/In-LFMP.

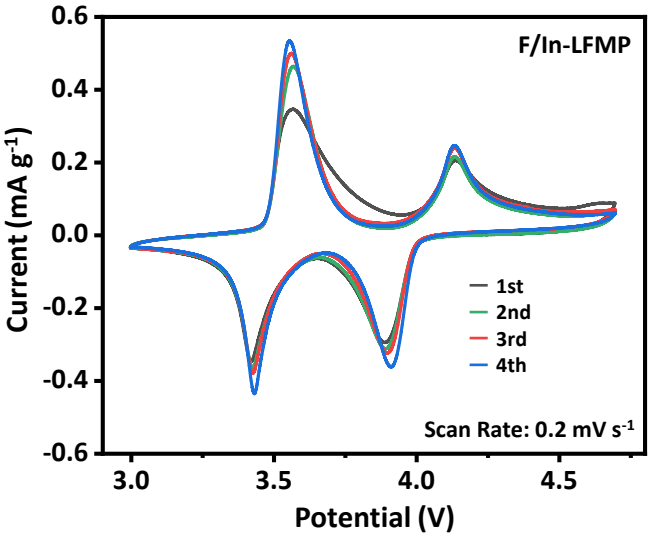

Fig. S3 CV curves of F/In-LFMP under a scan rate of 0.2 mV s^{-1}.

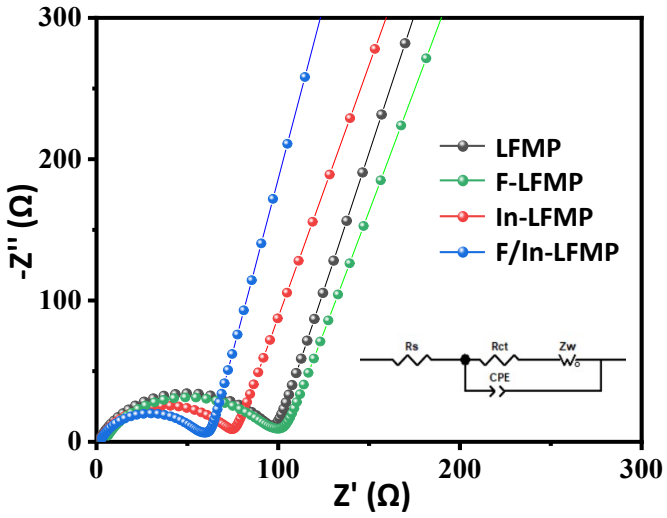

Fig. S4 Nyquist plots of distinct LFMP samples (Inset: equivalent circuit).

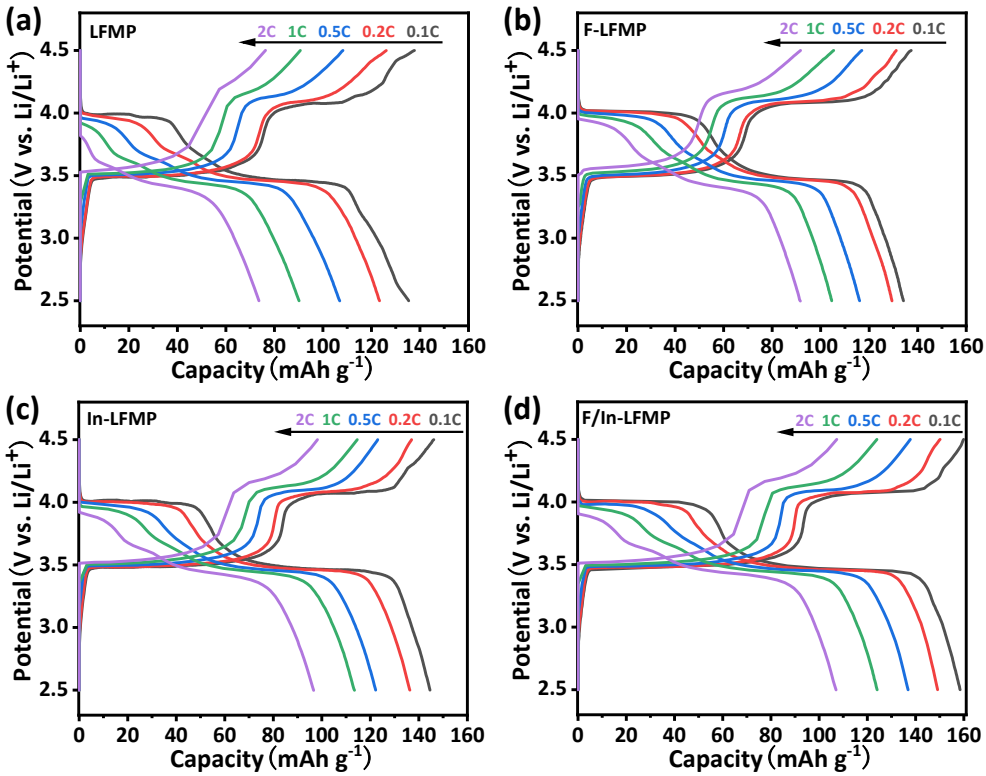

Fig. S5 Charge/discharge voltage profiles of (a) LFMP, (b) F-LFMP, (c) In-LFMP and (d) F/In-LFMP under varied current rates.

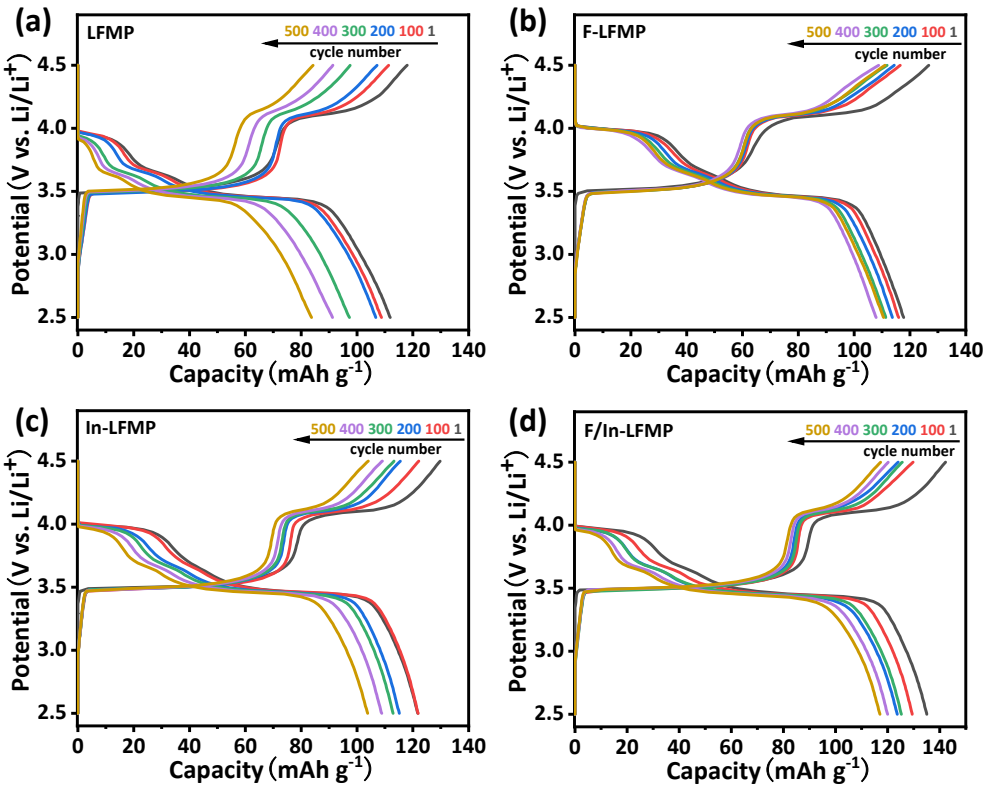

Fig. S6 Charge/discharge voltage curves of (a) LFMP, (b) F-LFMP, (c) In-LFMP and (d) F/In-LFMP at 0.5C for different cycles.

Samples	LFMP	F- LFMP	In- LFMP	F/In-LFMP
a /Å	6.0478	6.04483	6.04241	6.04293
b /Å	10.3784	10.3733	10.371	10.37025
c /Å	4.7188	4.7176	4.7199	4.71799
α= β= γ /°	90	90	90	90
Unit-cell Volume /Å^3	296.1825	295.8163	295.7765	295.6608

Table S1 The calculated lattice parameters of LFMP, F-LFMP, In-LFMP and F/In-LFMP by Rietveld refinement.

Samples	LFMP	F-LFMP	In-LFMP	F/In-LFMP
Bond Length/ Å				
Li-O(1)×1	2.20916	2.18481	2.26935	2.17602
Li-O(2)×1	2.18649	2.24828	2.21776	2.25918
Li-O(3)×1	2.11233	2.07505	2.09460	2.09982
Li-O(4)×1	2.23367	2.32860	2.38673	2.48783
Li-O(5)×1	2.20800	2.17830	2.17502	2.14004
Li-O(6)×1	2.10854	2.09342	2.05546	1.98736
Li-O Average	2.17637	2.18743	2.19982	2.19171

Table S2 Specific Li-O length data and average values of LFMP, F-LFMP, In-LFMP and F/In-LFMP by DFT calculations.