Supporting Information

Structural evolution and cycling performance enhancement of $LiFe_{0.5}Mn_{0.5}PO_4$ nanofibers as cathode materials for aqueous lithium-ion batteries

Shanbao Zou[a], Xinjian Qin[a], Wangsheng Yuan, Xinhai Yuan*, Wenjing Ji, Zhanfeng Zhang, Lijun Fu*, Yuping Wu[a,b]

[a] School of Chemistry and Molecular Engineering, State Key Laboratory of Materials-Oriented Chemical Engineering, and School of Energy Science and Engineering, Nanjing Tech University, Nanjing, Jiangsu, 211816, China.

b. Confucius Energy Storage Lab, School of Energy and Environment & Z Energy Storage Center, Southeast University, Nanjing 211189, China.

Email: xhyuan2022@njtech.edu.cn (X. Y.);

l.fu@njtech.edu.cn; lijunfufu@sina.com (L. F.)

1. Experimental Section

1.1 Material

Lithium nitrate ($LiNO_3$, 99%), Iron nitrate nonahydrate ($Fe(NO_3)_3·9H_2O$, 99%), Manganese(II) nitrate hexahydrate ($Mn(NO_3)_2·6H_2O$, 98%), Lithium sulfate (Li_2SO_4, 99%), Lithium trifluoroacetate (LiTFAC, 95%), Polyvinylpyrrolidone (PVP), N-methyl-2-pyrrolidone (NMP, 99%) and N,N-Dimethylformamide (DMF, 99%) were purchased from Aladdin. Phosphoric acid (H_3PO_4, 85%) was purchased from Shanghai National Pharmaceutical Co., Ltd. $LiTi_2(PO_4)_3$ (LTP), Glass fiber (GF/A, Whatman), activated carbon (AC), polyvinylidene fluoride (PVDF, HSV900) and Al foil were purchased from Saibo Electrochemical Materials. All materials were used without other purification.

1.2 Preparation of the $LiFe_{0.5}Mn_{0.5}PO_4$@C nanofibers electrode material

Typically, 1g of polyacrylonitrile (PVP, MW=1,300,000) was dissolved in 10 ml of DMF by constant stirring for 12 h to obtain a transparent solution. Subsequently, 6 mmol $LiNO_3$, 3 mmol $Fe(NO_3)_3·9H_2O$, 3mmol $Mn(NO_3)_2·6H_2O$ and 6mmol H_3PO_4 were added into the solution with sonication at room temperature to form a homogeneous solution. The as-prepared precursor solution was inhaled into a 10 mL syringe with a 21-gauge stainless steel needle for electrospinning. The electrospinning parameters were set as follows: the voltage of 15.0 kV between needle and collector with a distance of 30 cm and a flow rate of 0.05 mm min^{-1}. Finally, the elecctrospun nanofibers precursor was obtained and dried at 80 ℃ for 6 h. The as-prepared nanofibers precursor was first heated to 350 °C for 3 h and then heated to 700 °C for 6h in H_2/Ar_2 (9:1) with a heating rate of 5 °C min^{-1}. Finally, the $LiFe_{0.5}Mn_{0.5}PO_4$@C (LFMP@C) nanofibers electrode material were obtained after being cooled down to room temperature.

1.3 Preparation of Electrolytes

2 M Li_2SO_4 electrolyte was prepared by dissolving 2 mmol Li_2SO_4 into 1 ml water. 10 m, 20 m and 30 m LiTFAC electrolyte was prepared by dissolving 10, 20 and 30 mmol LiTFAC into 1 ml water, respectively.

1.4 Preparation of Electrode

For three-electrode cells, a mixture of LFMP@C, acetylene black and polytetrafluoroethylene (PTFE) in a mass ratio of 8:1:1 with ethanol was dried under an infrared lamp for 2 h, following pressed onto stainless steel mesh to form the cathode, with the mass loading around 3 mg cm^{-2}. The three-electrode cells were assembled with 1.5 mL mg^{-1} (calculated based on the mass of cathode) per cell.

For coin cell, the LFMP@C nanofibers cathode and LTP anode electrode slurries were prepared by dispersing the mixture of 80 wt% active materials, 10 wt% carbon black, and 10 wt% polyvinylidene fluoride with NMP in mixer at 900 rpm for 12h. The resulting electrode slurries was then coated on Al foil. Then, the electrodes were dried overnight at 80 °C in a vacuum oven and punched into 10 mm round disks. The mass loading for LFMP@C nanofibers cathode and LTP anode was also around 1.5 and 3 mg cm^{-2}, respectively. The LTP||LFMP@C full cell was assembled with an electrolyte usage of 20 μL mg^{-1} and 50 μL mg^{-1} (calculated based on the mass of LFMP@C), respectively. In order to reduce the dissolution of Mn, the P/N ratios for coin-type LFMP@C|| LTP full cells are set at ≈1.2. The C rate was calculated based on the theoretical capacity of LTP (1 C=138 mAh g^{-1}).

2. Material Characterization

The morphologies of the $LiFe_{0.5}Mn_{0.5}PO_4$@C nanofibers electrode material with elemental mapping was acquired by scanning electron microscope (JSM-7800F, JEOL, Japan) and transmission electron microscope (FEI Talos F200x). Crystal structure of the $LiFe_{0.5}Mn_{0.5}PO_4$@C nanofibers electrode material was confirmed on an X-ray Diffractometer (XRD, Bruker D8 Advance) with Cu Kα radiation (λ = 1.5408 Å). The element content of the electrolyte before and after cycling was confirmed on ICP optical emission spectrometry (Thermo Fisher iCAP PRO). X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS Ultra DLD instrument.

3. Electrochemical measurement

The electrochemical stability window of 2 M Li_2SO_4 and 30 m LiTFAC electrolyte was measured by linear sweep voltammetry (LSV) using a three-electrode cell with Al foil as the working electrode and counter electrode, Hg/Hg_2Cl_2 (SCE, with saturated KCl) as the reference electrode on the CHI600E electrochemical workstation at 0.1 mV

s^{-1}. Cyclic voltammetry (CV) was also collected on the CHI600E electrochemical workstation using three-electrode cell with LFMP@C pressed onto stainless steel mesh as the working electrode, carbon rod as the counter electrode and SCE as the reference electrode at 0.2 mV s^{-1}. The electrochemical performance of the LFMP@C cathode was determined by three-electrode cell with LFMP@C pressed onto stainless steel mesh as the working electrode, carbon rod as the counter electrode and SCE as the reference electrode using LAND CT3002A battery testers in a voltage range of 0–1.05 V. The cycle performance measurements of LFMP@C||LTP full cells were carried out using LAND CT3002A battery testers in a voltage range of 0–2 V for 30 m LiTFAC electrolyte. The electrochemical impedance spectroscopy (EIS) measurements of the three-electrode cell with LFMP@C pressed onto stainless steel mesh as the working electrode, carbon rod as the counter electrode and SCE as the reference electrode after different cycled were recorded on the CHI600E electrochemical workstation with a frequency range of 0.01 Hz to 100 kHz.

The Li^+ diffusion coefficient (D) was calculated from the Warburg region in the low frequency of the EIS plots based on the following equation:

$$D = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2}$$

where R is the gas constant, T is the absolute temperature, A is the surface area of the electrode, n is the number of electrons transferred, F is the Faraday's constant, C is the concentration of Li+ in the electrode, and σ is the Warburg coefficient which is related to the impedance Z' by the following equation:

$$Z^{'} = Rs + Rct + \sigma\omega^{-1/2}$$

2. Supplementary Figures

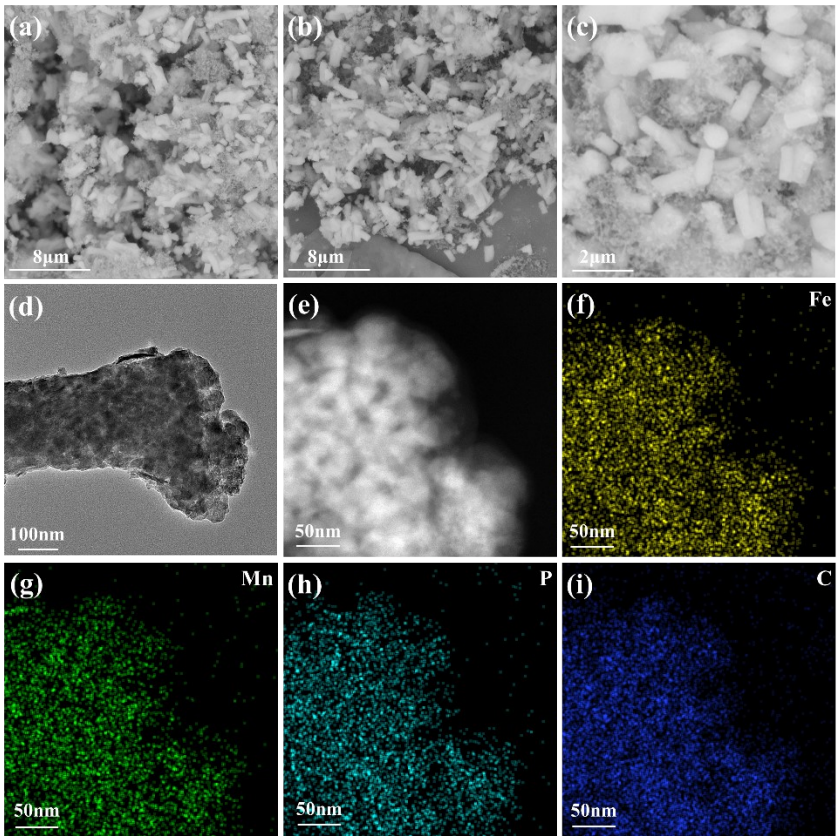

Fig. S1. Characteristics of LFMP@C nanofibers after 50 cycles in 2 M Li_2SO_4. (a–c) SEM images, (d) TEM image and (e-i) elemental mapping images of LFMP@C nanofibers.

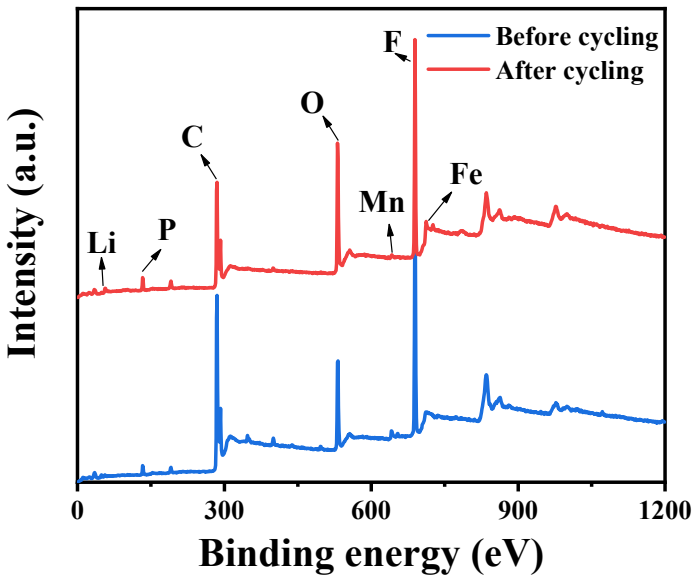

Fig. S2. XPS patterns of the LFMP@C nanofiber cathode before and after cycling.

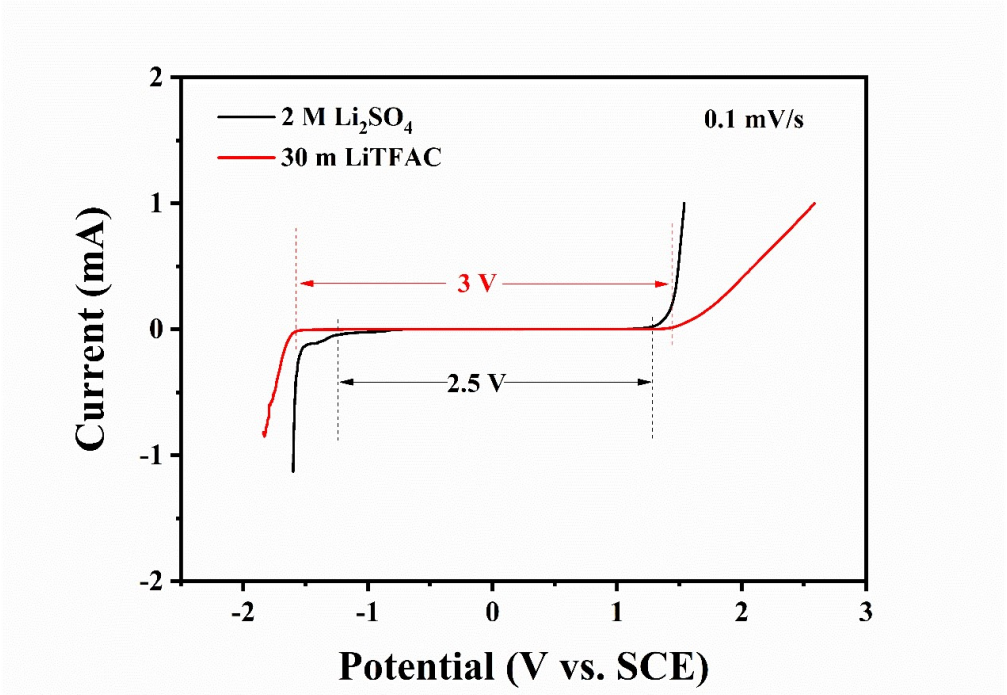

Fig. S3. The electrochemical stability windows of 30 m LiTFAC and 2 M Li_2SO_4 aqueous electrolytes measured by LSV curves at a scan rate of 0.1 mV s^{-1}.

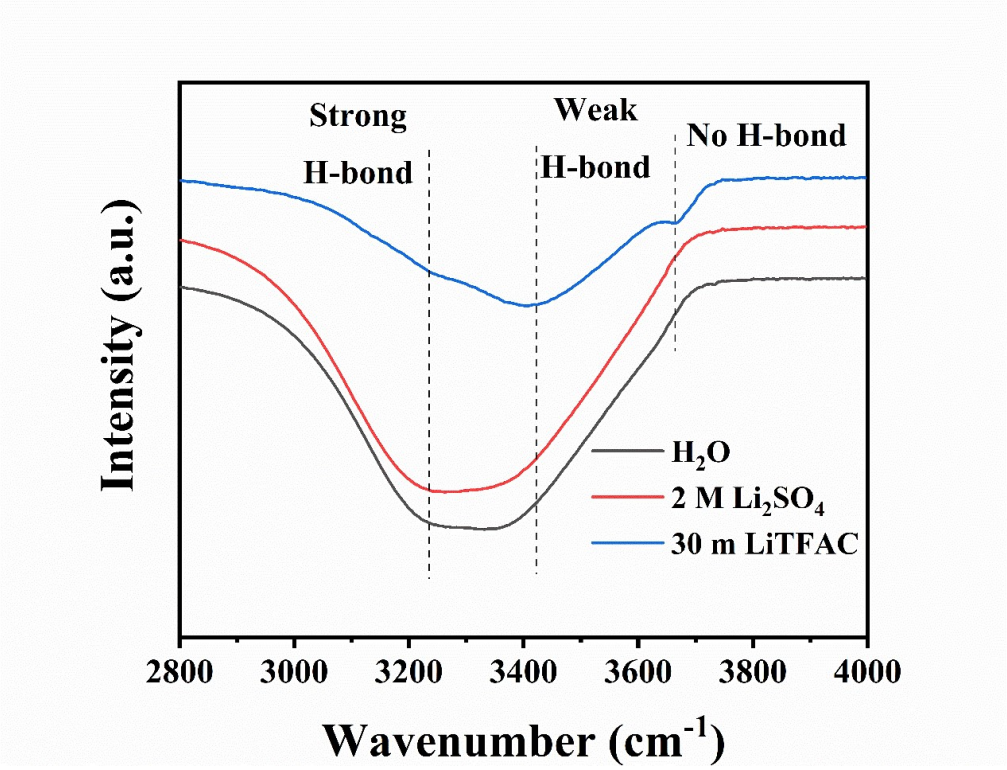

Fig. S4. Stretching modes of H_2O from FT-IR spectra for H_2O, 2 M Li_2SO_4 and 30 m LiTFAC.

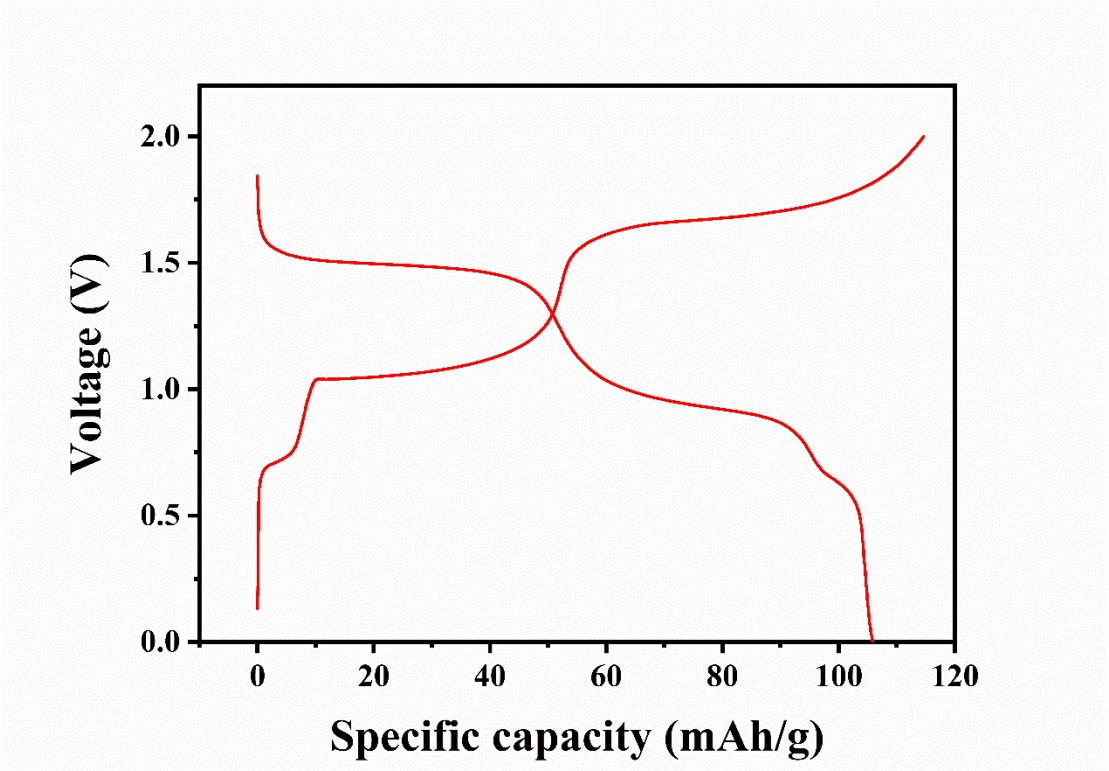

Fig. S5. The GCD curve of the LFMP@C||LTP full cell at 1 C in 30 m LiTFAC.

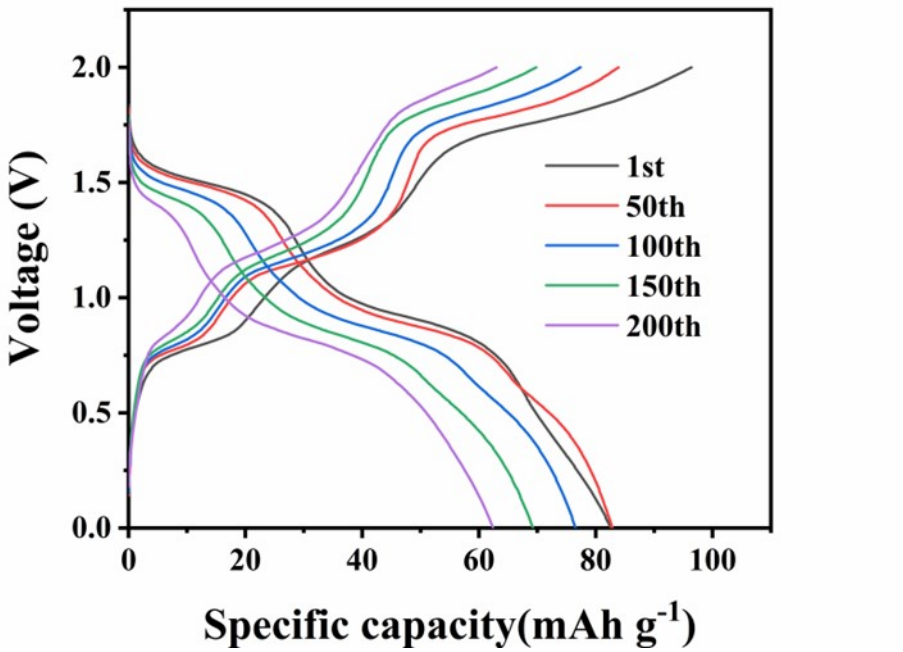

Fig. S6. The GCD curve of the LFMP@C electrode material after different cycled at 1 C in 30 m LiTFAC.

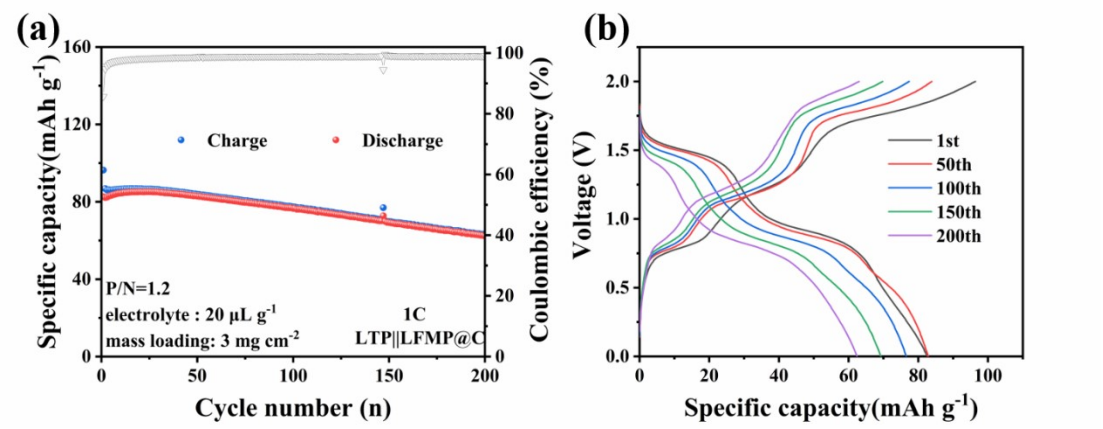

Fig. S7. The (a) cycling performance and (b) the GCD profiles of LFMP@C||LTP full cell at 1 C in 30 m LiTFAC, the capacity is calculated based on anode and the P/N ratio is 1.2.

Table S1. Elemental mapping is measured by TEM of LFMP@C nanofibers before and after cycled in 2 M Li_2SO_4.

	Fe	Mn	P	O	C
Before cycled	14.65	15.19	13.03	37.68	19.46
After cycled	0.33	0.23	0.35	22.30	76.80

Table S2. The Rct and D of LFMP@C cathode materials after different cycles in 2 M Li_2SO_4.

	Rct (Ω)	D (m^2 s^{-1})
1st	37.83	4.28×10^{-17}
10th	58.68	3.54×10^{-17}
20th	76.01	2.98×10^{-17}
30th	100.12	2.19×10^{-17}
40th	140.05	1.76×10^{-17}
50th	150.04	1.21×10^{-17}

Table S3. The Mn and Fe content in the 2 M Li_2SO_4 electrolyte before and after cycling.

ICP	Water	After cycling in 2 M Li_2SO_4	After cycling in 30 m LiTFAC
Mn (mg L^{-1})	2.1	16.1	3.3
Fe (mg L^{-1})	1.6	2.1	1.7